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BÉNARD CELLS IN LIQUIDS STUDIED BY OPTICAL METHODS

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(Communicated by Dr. K. R. Ramanathan, D.Sc., F.A.Sc.)

It is now well known that a thin layer of a fluid with unstable density distribution breaks up into a number of polygonal cells called Bénard cells. The most interesting example of this phenomenon in nature is the formation of certain types of strato-cumulus, alto-cumulus and cirrocumulus clouds, a fact first pointed out by Bénard himself and studied in considerable detail by Sir Gilbert Walker, Prof. Brunt and their students. Much experimental work has been done both on liquids and gases by many investigators including Bénard, Idrac, Terada, Avsec, Philips, Mal, K. Chandra and others. The problem has been mathematically treated by Lord Rayleigh, H. Jeffreys and Low. They have deduced criteria of stability and derived relations between the cell-dimensions and the depth of the layer.

The usual method of making the movements visible is to mix with the liquids shining particles of substances like aluminium, ' gold ' paint or lycopodium powder and tobacco or similar smoke for gases. Simple optical methods enable the phenomenon to be studied in much greater detail, as was pointed out some years ago by K. R. Ramanathan. Although optical methods were used by Bénard himself, they do not seem to have been used by later workers. In this paper, some observations on different liquids using optical methods are described.

A horizontal layer of liquid is obtained by floating it on clean mercury. The surface of a volatile liquid like ether or carbon-disulphide cools rapidly by evaporation resulting in an unstable distribution of density. With less volatile liquids like cocoanut oil, instability can be produced by placing the tray of mercury on a flat heater. A divergent beam of light from a point source is reflected at the mercury surface at nearly normal incidence, and the reflected light is received on a screen. A pattern is formed on the screen which is in a way an image of the local deviations of the optical thickness of the layer. Bright points and lines correspond to optically denser liquid and dark points and limes to optically lighter liquid. The liquid layer behaves roughly as a composite lens backed by a plane reflector. The pattern usually remains in good focus over a considerable distance from the layer.

Pictures were obtained by placing a photographic plate in the path of the reflected beam and giving a suitable short exposure. The thickness of the layer was measured with a micrometer screw provided with a long sharp pointer. A thermocouple in series with a galvanometer gave the temperature at the bottom of the layer. Once instability sets in, there were both vertical and horizontal temperature gradients and with such small thicknesses as were used, it was difficult to measure these.

Moderately viscous liquids such as water and some vegetable oils when heated uniformly at the bottom give the simplest patterns. With such liquids, only bright bordered cells were obtained showing ascending movement at the centre and descending movement at the boundary. The descending movement organises itself approximately along uniform continuous lines. The origin of instability being at the bottom, the upward movement is stronger than the downward and the latter is therefore distributed over a greater area. Viscosity slows up the movements and the patterns are stable. For making quantitative measurements stable liquids are convenient; it is easy to keep the depth of the layer constant and vary the temperature or to keep the temperature constant and vary the depth. (i) to (iii), Plate II, show the variation of cell-size with depth in a layer of cocoanut oil, the temperature of the bottom of the layer being constant at 100° C. The temperature of the top surface of the layer was not measured. Fig. 1 shows the area of cell plotted against the depth of the layer. The size of the cell is seen to increase rapidly with increasing depth. (iv) to (vi), Plate II, show the variation of the area of the cell with the temperature at the bottom of the layer the thickness of the layer of cocoanut oil being constant at 1.43 mm. The dark centres of rising columns are more concentrated with greater temperature gradients. With decreasing temperatures, the dark centres become less and less conspicuous and below about 40° C. the pattern disappears. Fig. 2 shows that the area of the cell at constant depth increases approximately linearly with temperature at the bottom of the layer.

Viscous liquids show a tendency to form long rolls as a result of movement. (vii), Plate II, shows the pattern obtained with an undisturbed layer of water. The dark spots are due to air bubbles which collect on the surface of mercury when the water is heated. (viii) shows the effect of movement when the air bubbles were swept out with a sheet of glass. The cells become elongated in the direction of movement and form rolls or columns which persist even on further heating. (ix) shows similar elongated cells with cocoanut oil.

Volatile liquids such as ether, benzene, alcohol, carbon disulphide and carbon tetrachloride give patterns easily, due to the cooling of the top

surface by evaporation, without any special heating at the bottom. (x) to (xii), Plate II, show the typical successive stages in the appearance of the pattern on the screen as a layer of ether floating on mercury gradually gets thinner. When the layer is thick, prominent dark canals and rapidly moving thin bright filaments make their appearance. The dark lines are regions at which the liquid ascends. As the thickness as well as the temperature diminish, the bright filaments converge to a series of points or lines surrounded by dark canals. As the film gets thinner the movements become less brisk, the dark canals get narrower and the bright spots in the middle of the cell get more concentrated and become connected together by bright lines. After a certain stage, the dark lines become invisible and we get bright bordered polygonal cells showing an ascending movement at the centre and descending movement at the boundaries. This stage persists

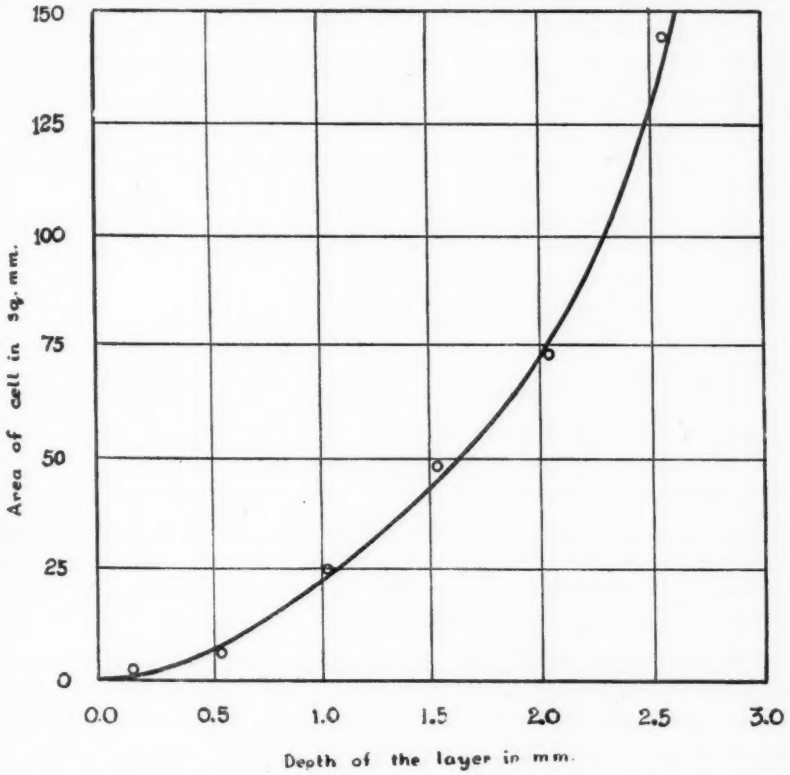

FIG. 1. Variation of cell area with depth of the layer. Cocoanut oil—Temperature at the 100° C.

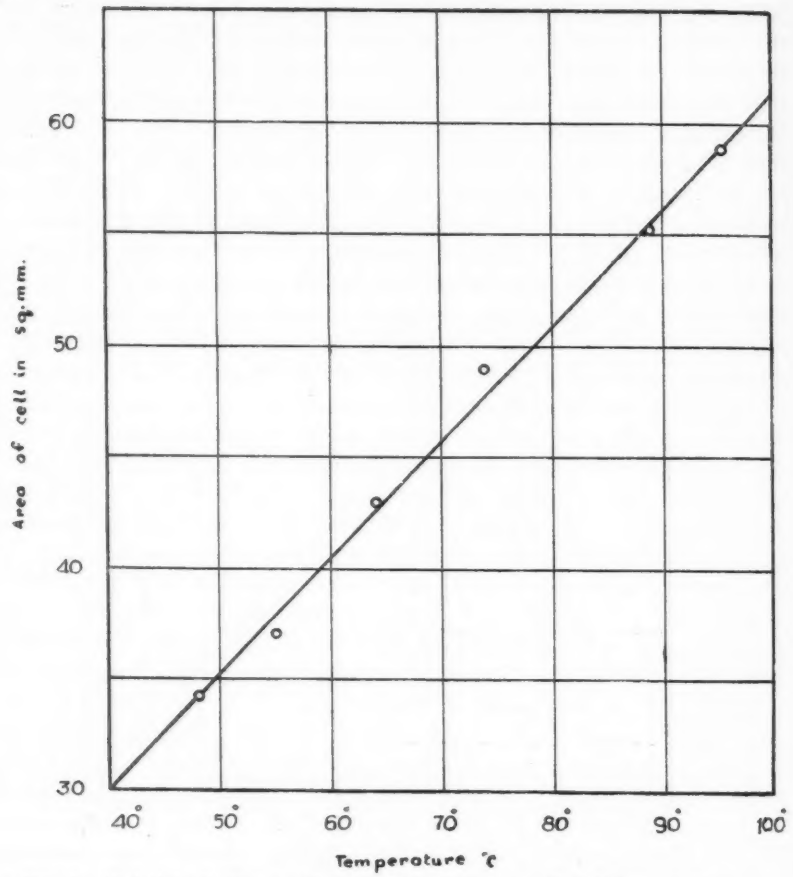

FIG. 2. Variation of cell area with temperature. Cocoanut oil—Thickness 1·43 mm.

as the layer gets thinner and breaks into a large number of cells of diminishing size—ultimately tending to become a network of more or less regular hexagonal cells of uniform size. Finally when the film thickness is about 0.1 mm. or less, the pattern disappears.

With ether, even with thin layers we do not get cells with uniformly bright boundaries. The bright lines tend to knot up and the knots become more prominent when the thickness increases. At one stage, (xi), Plate II, the dark and bright lines form an orthogonal system of intersecting cells. Even then, the knotting up at the descending bright points is rather more prominent. It appears that at small thicknesses the descending movement

due to sinking of cooled liquid is more vigorous while at larger thicknesses, the ascending movement becomes more vigorous. With increase in thickness of cell the effect of viscosity decreases and movements become more vigorous; any asymmetry in vertical movements gives rise to horizontal movements. The dark spots elongate and tend to join up. The advancing ends of the dark lines are seen to end abruptly. The pattern in ether is different from the pattern in cocoanut oil in that even in the thinnest stages, the bright lines in ether are not uniform in intensity but appear knotted. Descent is most vigorous at the knots. At a thickness of 0.85 mm., the dark spots have organised themselves into smooth lines. In fact in this picture both descents and ascents appear equally conspicuously. At greater thicknesses, at 1.85 mm. for example, the dark lines become much more conspicuous. With still greater thickness they become more and more sinuous and turbulent. When seen on the screen they present a most lively spectacle.

All volatile liquids show the same succession of changes, the briskness of movement increasing with diminishing viscosity and increasing coefficient of expansion. Any particular liquid also shows the same succession of patterns whatever the original thickness of the layer, provided it is larger than about 1 mm. The nature of the pattern seems to depend upon the thickness of the layer as well as the temperature gradient. It is possible to transform a particular pattern into the previous one by artificially heating from below.

With groundnut oil which is more viscous than cocoanut oil there is a tendency to form isolated perfectly circular cells, which later join up on further heating, (xiv) and (xv), Plate III. A careful examination of the plate shows that between neighbouring cells that have not joined up, there is a streaming movement of fluid. Within the bright bordered circular cell is seen a concentrated bright spot surrounded by a diffuse white ring. This effect is apparently due to diffraction of light from the edges of the cell and can be imitated by floating a small oil lens on water (xiii), Plate III. When drops of oil or mercury floating on water are examined by the same method, sharp bright spots are observed at the centre of the dark circle which represents the image of the drop, similar to the spot in " Poisson's disc experiment".

(xvi) and (xvii) show photographs of patterns obtained by the Schlieren method for ether and (xviii) for cocoanut oil. The similarity of the Bénard cells with cloud forms is more obvious from these pictures.

It was easy to observe the nature of the vertical circulation in an individual cell by watching the movement of fine particles of dust. In the case

of a cell with an ascending movement at the centre, a tiny dust particle is seen to shoot rapidly upwards at the centre and outwards towards the boundary where it sinks with diminished speed and almost creeps inwards towards the centre near the bottom of the layer.

Fig. 3 shows the vertical circulation in a cell, the number of arrows indicating the different speeds of the particle along its trajectory. The nature

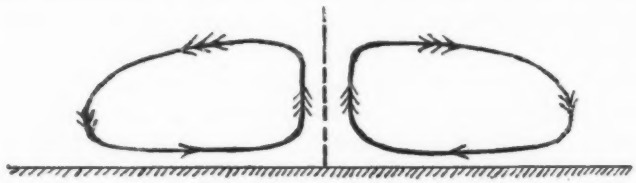

FIG. 3. Circulation in a Bénard Cell.

of the movement is well brought out in (xix) and (xx) of Plate III which show (1) a point source photograph of a thin layer of unstable carbon tetrachloride and (2) a photograph of a similar layer in which lycopodium dust had been put in. The lycopodium settles down in places of descent and is cleared out in places of ascent.

The author is thankful to Diwan Bahadur Dr. K. R. Ramanathan for suggesting the problem and taking interest in the work.

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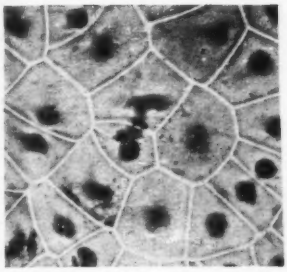
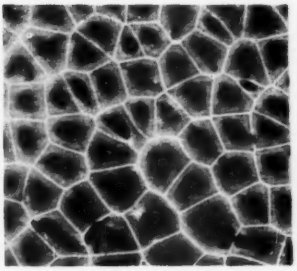


(i)



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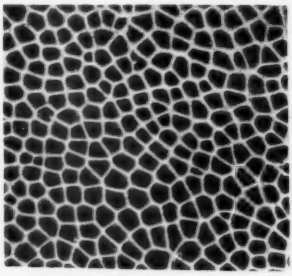

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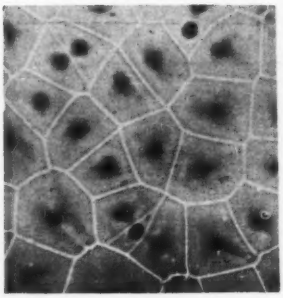

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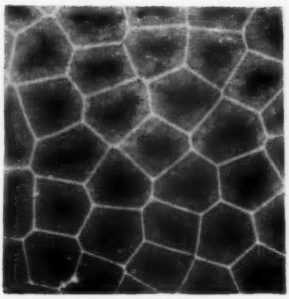

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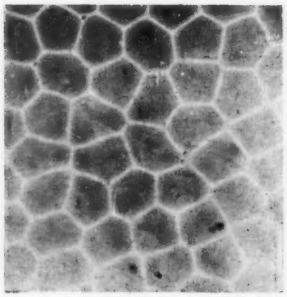

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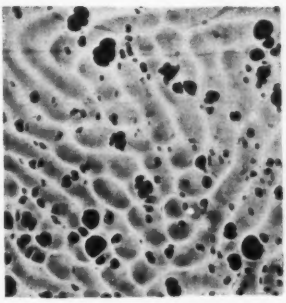

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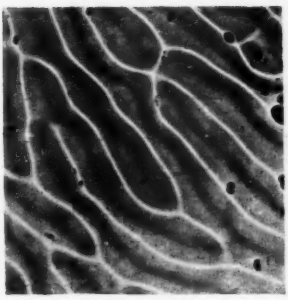

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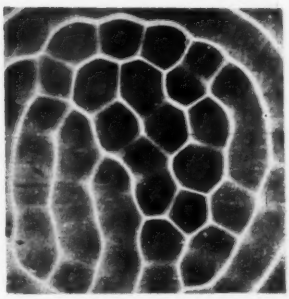
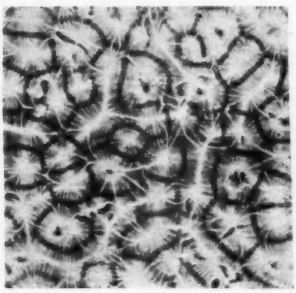
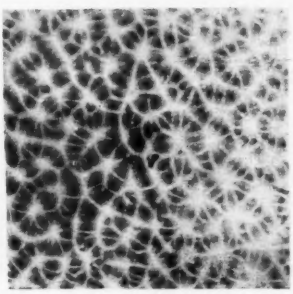


(ix)

(x)

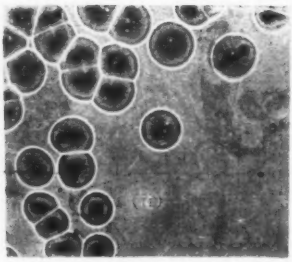


(xi)

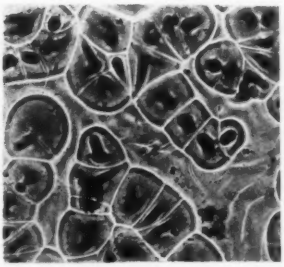


(xii)

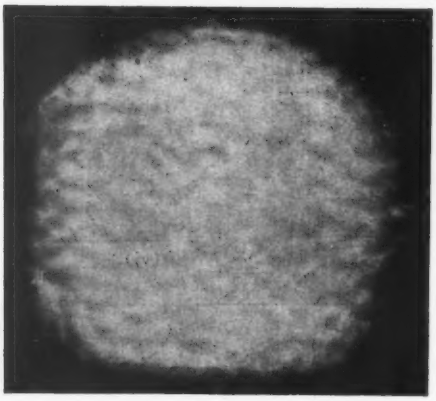
(xiii)



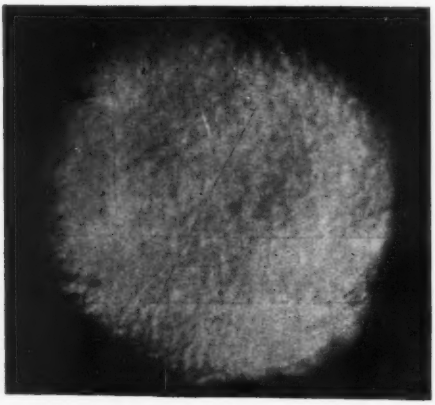
(xiv)



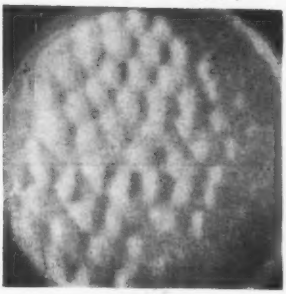
(xv)



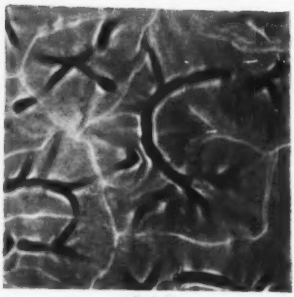
(xvi)



(xvii)



(xviii)



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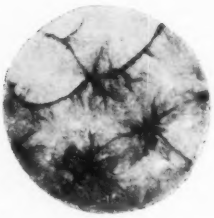

(xx)

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Explanation of Plates

Plate II

(i) Cocoanut Oil, 2 mm. thick.
(ii) Do. 1 mm. thick.
(iii) Do. 0·5 mm. thick.
(iv) Do. temperature of lower surface 95° C.
(v) Do. do. 74° C.
(vi) Do. do. 55° C.
(vii) Water, 1·23 mm. temp. 72° C.
(viii) Do. 1·73 mm. temp. 71° C with movement.
(ix) Cocoanut Oil, 1·5 mm. temp. 60° C.
(x) Ether, 1·2 mm.
(xi) Do. 0·85 mm.
(xii) Do. 0·65 mm.

Plate III

(xiii) Oil Lens on water.
(xiv) Groundnut Oil, 1·1 mm. 120° C.
(xv) Do. 1·1 mm. 148° C.
(xvi) Schlieren-photograph of ether, 1 mm. thick.
(xvii) Do. of ether, 0·5 mm. thick.
(xviii) Do. of Cocoanut Oil, 0·7 mm. thick.
(xix) Carbon tetrachloride ; point-source photograph.
(xx) Do. with lycopodium powder deposited in middle of cells.

NUCLEAR OXIDATION IN THE FLAVONE SERIES

Part XVIII. Oxidation of Acacetin and Related Flavones

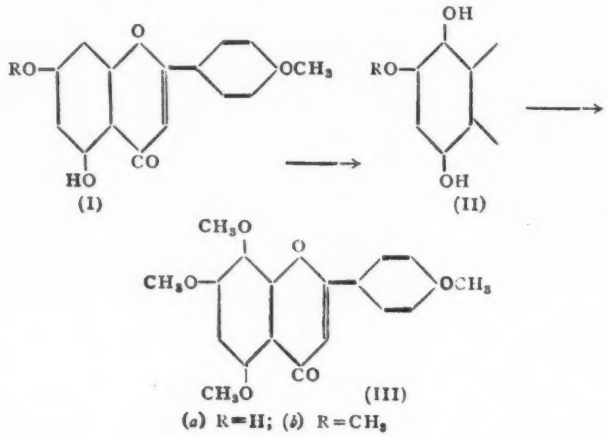
By K. Visweswara Rao, T. R. Seshadri and N. Viswanadham

(From the Department of Chemistry, Andhra University, Waltair)

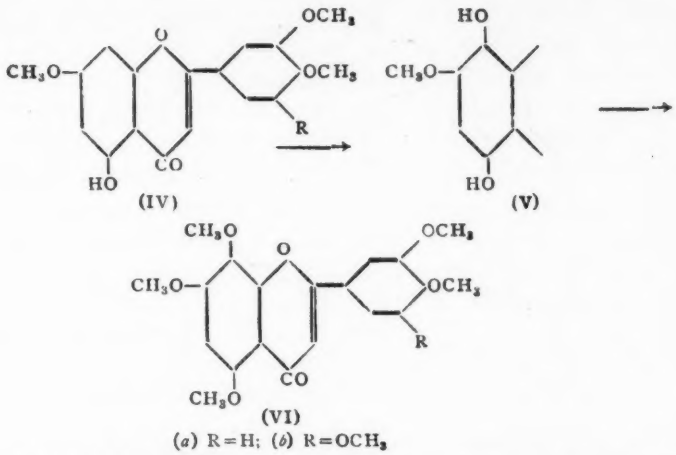
Received November 23, 1948

This paper is a continuation of Part II[1] wherein the oxidation of chrysin and tectochrysin to norwogonin and isowogonin was described. With the object of preparing directly 5:7:8:4′-tetrahydroxy flavone (isoscutellarein) which is the next higher member in the norwogonin series and which does not seem to have been obtained pure so far, oxidation of apigenin was carried out with alkaline persulphate. But the experiment was not successful. The yield of the product was extremely small and it could not be purified even after repeated trials. Hence the work was not pursued further with luteolin and tricetin. It is our experience that a free hydroxyl group in the 4′ and 3-positions are detrimental to smooth oxidation with persulphate.

But acacetin (I*a*) and its 7-methyl ether (I*b*) underwent oxidation very satisfactorily and the products (II) could be methylated to yield 5:7:8:4′-tetramethoxy flavone (III), isoscutellarein-tetramethyl ether which was earlier obtained by a longer route.[2] The same reactions could be repeated with luteolin (IV*a*) and tricetin (IV*b*) partial methyl ethers with the 5-hydroxyl free and thus the partially and fully methylated ethers of all the flavones



(*a*) R=H; (*b*) R=CH_3

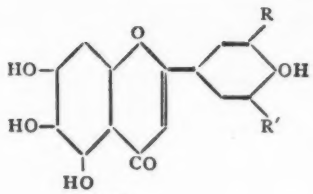


(*a*) R=H; (*b*) R=OCH₃

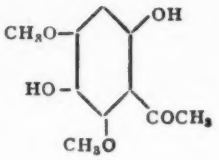
with the 5:7:8-arrangement of hydroxyl groups could be easily prepared. The higher members of this series were not described earlier. They could now serve as useful reference compounds in the case of new discoveries.

Demethylation of norwogonin methyl ethers with hydriodic acid definitely produces isomeric change into baicalein. Though the transformation may be slow and may not be considerable under mild conditions it cannot be altogether avoided (see Sastri and Seshadri[2] for discussion). Using aluminium chloride, however, for the demethylation, the successful preparation of norwogonin from its methyl ethers was reported.[2] This method has not succeeded with the higher members.

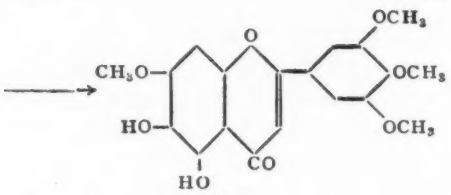
In view of the easy preparation of the partial methyl ethers (II and V) the possibility of their use in another direction suggested itself. By boiling them with hydriodic acid for over two hours the corresponding hydroxy flavones of the 5:6:7-hydroxy (baicalein) series could be obtained in satisfactory yields. This offers a simpler alternative method of preparing scutellarein[3] (VII*a*) and 6-hydroxyluteolin[4] (VII*b*) than those described before. Similarly can be obtained the highest member, 6-hydroxytricetin (VII *c*) which has not been described so far; hence its properties and those of its derivatives are given here in detail. For purposes of verification the older method of preparation has also been used. The condensation of 2:5-dihydroxy-4:6 dimethoxy acetophenone (VIII) with the anhdydride and sodium salt of trimethyl gallic acid yields 5:6-dihydroxy-7:3′:4′:5′-tetramethoxy flavone (IX) owing to partial demethylation taking place during the reaction. Methylation of it produces the hexamethyl ether which is identical with the sample obtained by the newer method.



(VII)



(VIII)



(IX)

(*a*) R = R′ = H; (*b*) R = OH, R′ = H; (*c*) R = R′ = OH

Experimental

Acacetin.—The following is a modification of the original method of synthesis.[5] Phloracetophenone (5 g.) was condensed with anisic anhydride (35 g.) and sodium anisate (10 g.) under the conditions of Allan-Robinson reaction. After hydrolysis and working up, a yellowish brown solid (9 g.) was obtained which melted indefinitely between 140 and 160°. It was dissolved in 5% sodium carbonate (400 c.c.) and refluxed for 2 hours. After cooling, the solution was acidified when a yellowish brown solid was precipitated (5 g.). Crystallisation from alcohol yielded pure acacetin (3·5 g.) as pale straw yellow needles melting at 261–63°. The acid filtrate slowly deposited anisic acid.

5 : 7 : 8-*Trihydroxy*-4′-*methoxy-flavone* (II *a*).—A solution of acacetin (1 g.) in aqueous potassium hydroxide (1·5 g. in 30 c.c. of water) was treated dropwise while stirring with a solution of potassium persulphate (1·5 g. in 50 c.c.) in water during the course of two hours. The colour of the solution changed from yellow to dark greenish brown and finally brown red. After keeping for 24 hours it was acidified and the unchanged acacetin that separated out was filtered off and the filtrate extracted twice with ether. The clear brown aqueous solution was treated with sodium sulphite (3 g.) and concentrated hydrochloric acid (25 c.c.) and kept at 80–85° for 30 minutes with occasional stirring. The yellow solid that separated out on cooling was filtered and washed; from the filtrate some more was obtained by extraction with ether. Yield, 0·35 g. Crystallisation from a mixture of ethyl acetate and petroleum ether yielded yellow long rectangular plates

melting at 275–77°. (Found: C, 63·9; H, 3·7; $C_{16}H_{12}O_6$ requires C, 64·0; H, 4·0%.) It was sparingly soluble in ethyl acetate and more soluble in alcohol. The alcoholic solution gave a greenish brown colour with a drop of ferric chloride and the colour changed to deep reddish brown with a few more drops. In 5% sodium hydroxide it readily dissolved to a deep brown red solution which quickly changed to pale blue on shaking with air.

The trihydroxy compound (0·1 g.) was methylated by boiling with dimethyl sulphate (0·3 c.c.) and potassium carbonate (3 g.) in dry acetone (20 c.c.) for 30 hours. The methyl ether crystallised from alcohol in the form of colourless needles melting at 209–10° alone or in admixture with an authentic sample of 5:7:8:4′-tetramethoxy flavone.[2] By boiling the trihydroxy compound with acetic anhydride and hydroiodic acid for over two hours complete conversion into scutellarein was effected.

7:4′-*Dimethoxy-5-hydroxy-flavone* (*I b*).—A solution of acacetin (1·5 g.) in dry acetone (50 c.c.) was treated with dimethyl sulphate (0·55 c.c.) and potassium carbonate (5 g.). After refluxing for 6 hours the solvent was distilled off and the residue treated with water; the brownish yellow solid left behind was filtered off, washed and purified by crystallisation from ethyl acetate from which it separated as pale brown rectangular plates melting at 171–72° (*cf.* Perkin[6]). Yield, 1·3 g.

5:8-*Dihydroxy*-7:4′-*dimethoxy-flavone* (*II b*).—The above dimethyl ether of apigenin (1 g.) was dissolved in a mixture of pyridine (20 c.c.) and aqueous potassium hydroxide (1·5 g. in 25 c.c.). The clear bright yellow solution was treated dropwise with a solution of potassium persulphate (1·5 g. in 50 c.c.) with continuous stirring. The deep greenish brown solution after allowing to stand for 24 hours, was worked up as described in an earlier experiment. The bright yellow crystalline solid which separated out during the hydrolysis was filtered and some more obtained from the filtrate on extraction with ether. Yield 0·3 g. It crystallised from excess of ethyl acetate in the form of yellow flat needles melting at 265–67°. (Found: C, 65·0; H, 4·2; $C_{17}H_{14}O_6$ requires C, 65·0; H, 4·5%.) It was sparingly soluble in alcohol, ethyl acetate and acetone and moderately in glacial acetic acid. In alcoholic solution it gave with ferric chloride a green colour which rapidly changed to deep brown. In 5% aqueous sodium hydroxide it readily dissolved to a deep reddish brown solution.

The above dihydroxy flavone (0·2 g.) was methylated using dimethyl sulphate (0·2 c.c.) and potassium carbonate (2 g.). The tetramethyl ether crystallised from alcohol in the form of colourless needles melting at 209–10° and was identical with the sample already described.

3′ : 4′-*O-Dimethyl luteolin*.—Phloracetophenone (5 g.) was intimately mixed with veratric anhydride (35 g.) and sodium veratrate (12 g.) and heated at 180–90° under reduced pressure for 5 hours. The reaction product was refluxed with 10% alcoholic potash (150 c.c.) for 30 minutes and the solvent distilled off under reduced pressure. The residue was dissolved in water (500 c.c.) and the clear solution saturated with carbon dioxide when the crude 3-veratroyl derivative separated out. Yield, 7 g. It was filtered, washed with water and refluxed with 5% sodium carbonate (300 c.c.) for 2 hours and the solution acidified. The precipitated flavone was filtered and washed twice with hot water and crystallised from alcohol. It formed pale yellow flat needles melting at 283–85°. (Found: C, 64·6; H, 4·8; $C_{17}H_{14}O_6$ requires C, 65·0; H, 4·5%.) Yield, 3 g. It was sparingly soluble in alcohol and the solution gave a deep violet brown colour with ferric chloride.

Luteolin-7 : 3′ : 4′-*trimethyl ether* (*IV a*).—A mixture of dimethyl luteolin (3 g.), dimethyl sulphate (1 c.c.), potassium carbonate (5 g.) and acetone (100 c.c.) was refluxed for 6 hours. The product was isolated by distilling off the solvent and adding water (150 c.c.). It crystallised from alcohol as pale yellow needles melting at 169–70°. Yield, 2·4 g. Purification through the potassium salt[7] did not change the melting point. Perkin and Horsfall[8] who obtained it along with a related nuclear methylated product and experienced considerable difficulty in purification, recorded its melting point as 161–63°.

5 : 8-*Dihydroxy*-7 : 3′ : 4′-*trimethoxy flavone* (*V a*).—The above trimethyl luteolin (2 g.) was oxidised in a mixture of pyridine (30 c.c.) and potassium hydroxide (2 g. in 20 c.c.) with aqueous potassium persulphate (2·5 g. in 100 c.c.) added during the course of two hours. The product was isolated after hydrolysis with concentrated hydrochloric acid (40 c.c.) at 100° for 30 minutes. It was crystallised first from a mixture of acetone and ethyl acetate and subsequently from pyridine from which it came out in the form of yellow feathery plates melting at 254–55°. (Found: C, 62·5; H, 5·0; $C_{18}H_{16}O_7$ requires C, 62·8; H, 4·7%.) Yield, 0·8 g. It was very sparingly soluble in alcohol, acetone and ethyl acetate and moderately so in pyridine. In alcoholic solution it gave a greenish brown colour with a drop of ferric chloride solution and with more turned deep brown red. In 5% alkali it dissolved to a deep brown red solution.

The diacetate prepared by boiling with acetic anhydride and pyridine crystallised from alcohol as colourless needles melting at 216–17°.

5 : 7 : 8 : 3′ : 4′-*Pentamethoxy flavone* (*VI a*).—The dihydroxy compound (0·2 g.) was methylated in acetone solution (25 c.c.) with dimethyl sulphate

(0·5 c.c.) and potassium carbonate (3 g.) by refluxing for 30 hours. The methyl ether crystallised from a mixture of benzene and ligroin in the form of colourless needles melting at 206–7°. (Found: C, 64·2; H, 5·7; $C_{20}H_{20}O_7$ requires C, 64·5; H, 5·4%.) It was insoluble in aqueous sodium hydroxide and did not give any colour with ferric chloride.

5: 6: 7: 3′: 4′-*Pentahydroxy flavone* (*VII b*).—The dihydroxy compound (0·5 g.) was demethylated in acetic anhydride solution (6 c.c.) with hydriodic acid (10 c.c.) by refluxing for 2½ hours. The pentahydroxy compound crystallised from a mixture of ethyl acetate and benzene in the form of yellow short prisms melting with decomposition at 315°, yield 0·25 g. In all its properties and reactions it agreed with 5: 6: 7: 3′: 4′-pentahydroxy flavone already described by Murti and Seshadri.[4]

The penta-acetate prepared by the reaction of acetic anhydride and pyridine crystallised from alcohol as colourless narrow rectangular plates melting at 225–26°.

5: 7-*Dihydroxy*-3′: 4′: 5′-*trimethoxy flavone*.[9]—This compound was made by the condensation of phloracetophenone (5 g.) with O-trimethyl gallic anhydride (40 g.) and sodium O-trimethyl gallate (12 g.). In a number of experiments the product was invariably the corresponding 3-acyl derivative and it was therefore subjected to hydrolysis by refluxing with 5% sodium carbonate for 2 hours. The dihydroxy compound crystallised from alcohol in the form of pale yellow needles melting at 269–70°. Yield, 1·2 g.

Tricetin tetramethyl ether (*IV b*).—This has not been reported earlier and is now made by the partial methylation of the above 5: 7-dihydroxy compound.

A mixture of 5: 7-dihydroxy-3′: 4′: 5′-trimethoxy flavone (3·4 g.), dimethyl sulphate (1 c.c.), potassium carbonate (10 g.) and anhydrous acetone (100 c.c.) was refluxed for 6 hours. The solvent was distilled off, the residue treated with water and the solid filtered. It crystallised from alcohol in the form of colourless rectangular plates melting at 195–96°. Yield, 3·2 g. (Found: C, 63·8; H, 5·4; $C_{19}H_{18}O_7$ requires C, 63·7; H, 5·0%.) In contrast with other 5-hydroxy compounds of this series, this tetramethyl tricetin is quite colourless. It gave a deep reddish brown colour with alcoholic ferric chloride and on heating with aqueous sodium hydroxide, the solid turned yellow in colour.

5: 8-*Dihydroxy*-7: 3′: 4′: 5′-*tetramethoxy flavone* (*V b*).—The above tricetin tetramethyl ether (2 g.) was oxidised in a mixture of pyridine (40 c.c.) and aqueous potash (2 g. in 40 c.c.) with a solution of potassium persulphate

2·2 g. in 100 c.c.). The product was worked up as usual by removing the unchanged compound and hydrolysing with concentrated hydrochloric acid (40 c.c.). The resulting yellow solid was crystallised from ethyl acetate. It formed bright yellow elongated rectangular prisms melting at 227–29°. (Found: C, 60·7; H, 5·0; $C_{19}H_{18}O_8$ requires C, 61·0; H, 4·8%.) Yield, 0·8 g. It was sparingly soluble in alcohol and the solution gave a brown red colour with ferric chloride deepening with excess. It readily dissolved in aqueous sodium hydroxide to a deep reddish brown solution.

5:7:8:3′:4′:5′-*Hexamethoxy flavone* (*VI b*).—The above dihydroxy compound (0·2 g.) was boiled for 30 hours in acetone solution (20 c.c.) with dimethyl sulphate (0·5 c.c.) and potassium carbonate (5 g.). The methyl ether crystallised from alcohol in the form of colourless narrow rectangular plates melting at 196–98°. (Found: C, 62·7; H, 5·8; $C_{21}H_{22}O_8$ requires C, 62·7; H, 5·5%.) It was insoluble in aqueous alkali and did not give any colour with ferric chloride.

5:6:7:3′:4′:5′-*Hexahydroxy flavone* (*VII c*).—The hydroxy compound (V *b*) described above (0·5 g.) was demethylated with acetic anhydride (6 c.c.) and hydriodic acid (10 c.c.) by refluxing for 2½ hours. The reaction mixture was cooled and poured into water containing sulphur dioxide. The yellowish solid was filtered, washed well and crystallised from a mixture of ethyl acetate and acetone. It formed yellow prisms which did not melt below 340° but darkened at about 320°. (Found: C, 56·2; H, 3·3; $C_{15}H_{10}O_8$ requires C, 56·6; H, 3·1%.) Yield, 0·25 g.

5:6:7:3′:4′:5′-*Hexamethoxy flavone*.—The hexamethoxy flavone (0·2 g.) was methylated in acetone medium (30 c.c.) with dimethyl sulphate (0·1 c.c.) and potassium carbonate (5 g.) by boiling for 30 hours. The methyl ether crystallised from benzene-ligroin mixture in the form of colourless rectangular plates melting at 151–52°. (Found: C, 63·0; H, 5·8; $C_{21}H_{22}O_8$ requires C, 62·7; H, 5·5%.)

5:6-*Dihydroxy*-7:3′:4′:5′-*tetramethoxy flavone*.—An intimate mixture of 4:6-dimethoxy-2:5-dihydroxy-acetophenone (Sastri and Seshadri[3]) (2 g.), O-trimethyl gallic anhydride (10 g.) and sodium O-trimethyl gallate (4 g.) was heated under reduced pressure at 180–90° for 5 hours. The product was worked up as usual and the crude flavone derivative precipitated by passing carbon dioxide. It was directly hydrolysed by refluxing with 5% sodium carbonate (100 c.c.) and alcohol (20 c.c.) for 2 hours. The alkaline solution was acidified, the brown solid filtered and washed well with hot water. Crystallisation from ethyl acetate yielded pale yellow glistening rectangular prisms melting at 265–68°. (Found: C, 61·0; H, 5·2;

$C_{19}H_{18}O_8$ requires C, 61·0; H, 4·8%.) It was sparingly soluble in alcohol and the solution gave a deep green colour with ferric chloride. In 5% aqueous sodium hydroxide it formed a yellowish brown solution with a bluish green precipitate.

On boiling with excess of dimethyl sulphate and potassium carbonate in acetone medium, this dihydroxy compound yielded the methyl ether which crystallised from benzene-ligroin mixture in the form of colourless rectangular plates melting at 151–52°. The mixed melting point with the 5: 6: 7: 3′: 4′: 5′-hexamethoxy flavone already described was not depressed.

Summary

Apigenin does not undergo persulphate oxidation satisfactorily. But acacetin, its monomethyl ether and analogous higher members do so. By the methylation of the products (quinols) the fully methylated ethers of iso-scutellarein, 8-hydroxyluteolin and 8-hydroxytricetin could be readily obtained. Demethylation of the quinols or their methyl ethers with aluminium chloride is not successful. Boiling with hydriodic acid produces isomeric change yielding conveniently scutellarein and the higher members. 6-Hydroxy-tricetin and its derivatives are newly described.

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   Robinson and Schwarzenbach .. *J. C. S.*, 1930, 822.
   Sastri and Seshadri .. *Proc. Ind Acad. Sci.*, A, 1946, **23**, 262.
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SOME IMPORTANT ETHYL AND ETHYL-METHYL ETHERS OF FLAVONOLS

Transformation of Quercimeritrin into O-Tetraethylrhamnetin

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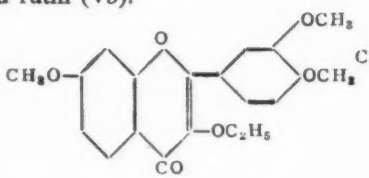
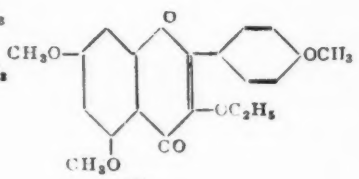
Ethylation as a technique has not been as widely adopted as methylation in the study of naturally occurring organic compounds. However, earlier workers like Herzig[1] and Perkin[2] prepared ethyl ethers of flavonols in a number of cases using ethyl iodide. The special reason might have been that, by using ethyl iodide, ethylation could be carried to completion whereas with the use of methyl iodide the resistant 5-hydroxyl group was left out. The higher boiling point of ethyl iodide and consequently the use of a higher temperature should account for this advantage.

More recently Seshadri and co-workers have employed ethylation as a convenient means for the study of partial methyl ethers and glucosides of hydroxy flavones and this has enabled the work to be carried out with greater ease and definiteness. The main examples are patuletin,[3] calycopterin,[4] tambuletin,[5] gossypin,[6] populnin[7] and hibiscitrin.[8]

There has been some difficulty in preparing synthetically most of the ethyl ethers of flavonols because ethoxyacetonitrile was not easily available. The recent simplified synthesis of this compound by Row and Thiruvengadam[9] has enabled the preparation of various substituted ω-ethoxy acetophenones to be easily made. From these could be readily prepared flavonols with an ethoxyl in the 3-position and methoxyls in the other positions. The following compounds have been made in this connection: 3-ethoxy-7: 3′: 4′-trimethoxy flavone (I), 3-ethoxy-5: 7: 4′-trimethoxy flavone (II) and 3-ethoxy-5: 7: 3′: 4′-tetramethoxy flavone (III). These can serve as reference compounds for the study of 3-glycosides such as kæmferitrin (IV), quercitrin (V*a*) and rutin (V*b*).



(I)



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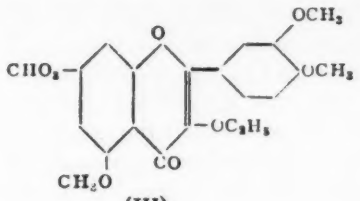

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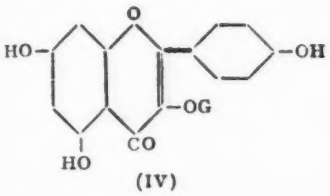

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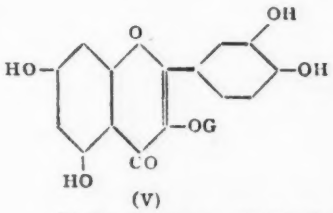


(V)

(*a*) G = Rhamnose. (*b*) G = Rutinose.

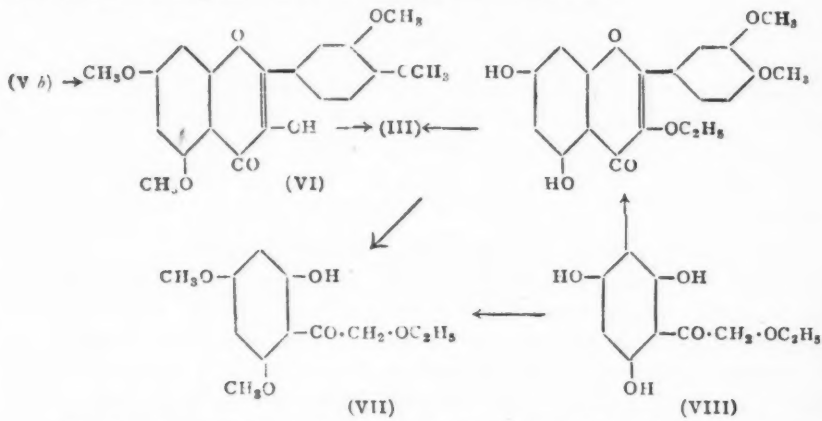
The case of rutin is now studied as a suitable example. It was discovered by Weiss[10] in the leaves of rue (*Ruta graveolens*, Linn.) and has subsequently been isolated from other sources as well, notably from *Sophora japonica*, buckwheat (*Fagopyrum esculentum*) and tobacco. Recently it has assumed great importance on account of its capacity to act as vitamin P and is being produced in U.S.A. in large quantities from buckwheat as the source. Zwenger and Dronke[11] showed that it was not identical with quercitrin but differed from it in that it gave on hydrolysis one molecule of quercetin and two molecules of sugar. Schmidt[12] proved that of the two molecules of sugar one was glucose and the other rhamnose. He assigned to rutin the formula $C_{27}H_{30}O_{16}$. It is now known that the sugar is a biose, termed rutinose.

The position of the sugar residue in rutin was first investigated by Attree and Perkin.[13] They methylated rutin with diazomethane when they obtained a yellowish orange resinous mass. This was hydrolysed with 7% sulphuric acid and the resulting product compared with 3-hydroxy-5:7:3′:4′-tetramethoxy flavone (VI).[14] The two were found to be identical. Hence they concluded that rutin is a 3-glycoside.

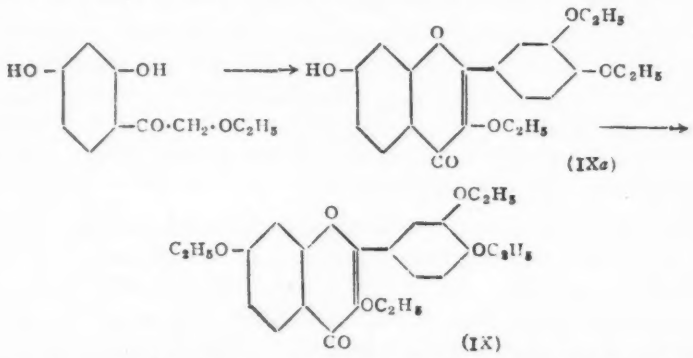
The concerned 3-hydroxy compound does not undergo degradation satisfactorily and was originally synthesised by the method of Kostanecki[14] involving several steps. On the other hand its ethyl ether suffers smooth fission and this mixed ether as well as its fission ketone can be synthesised readily and could therefore serve better as reference compounds.

The methylation of rutin (V*b*) has now been effected conveniently with dimethyl sulphate in acetone solution in the presence of anhydrous potassium

carbonate. The product is subjected to hydrolysis with 7% sulphuric acid and ethylation with diethyl sulphate. The mixed ethyl-methyl ether thus obtained is found to be identical with a synthetic sample of 3-ethoxy-5:7:3′:4′-tetramethoxy flavone (III). Further when this ether is subjected to fission with alcoholic potash, it yields the ketone (VII) which is identical with ω-ethoxy-2-hydroxy-4:6-dimethoxy acetophenone obtained from ω-ethoxy phloracetophenone (VIII) by partial methylation.

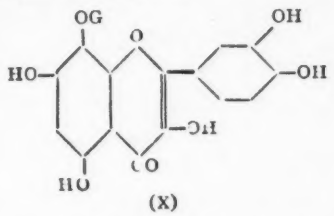


As already mentioned, though earlier workers ethylated certain naturally occurring flavonols, these ethers have not till now been obtained directly by synthetic means probably because the required ω-ethoxy acetophenones were not available. As a typical example of fully ethylated ethers the synthesis of fisetin tetraethyl ether (IX) has been carried out now.

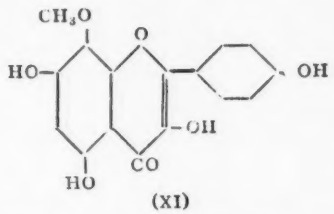


In a recent paper by Rao and Seshadri[6] it has been pointed out how the ethylation of flavonol glycosides is itself a very useful operation and how the

ethylation product, after hydrolysis and further methylation, can be conveniently used for purposes of establishing the constitution of glycosides. This enables also a correlation to be effected between glycosides and partial methyl ethers. The case of gossypin (X) and tambuletin (XI) was studied by them and reported.

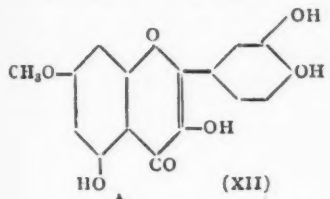


(X)



(XI)

A more closely related pair would be rhamnetin (XII) and quercimeritrin (XIII). The constitution of quercimeritrin as the 7-monoglucoside of quercetin has been discussed in detail in a recent publication from this laboratory.[15] Rhamnetin (XII) is a monomethyl ether of quercetin. The position of the ether group as 7 was arrived at by Perkin and Allison[16] based on the following considerations. Alkali fission gave rise to protocatechuic acid and monomethyl phloroglucinol. This indicated that the methoxyl was in the 5- or 7-position. But the production of quercetin tetramethyl ether (XIV) from rhamnetin (XII) by the action of methyl iodide showed that the resistant 5- hydroxyl was free and that the 7-position therefore carried the ether group.



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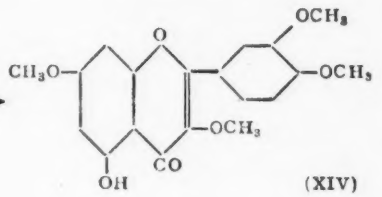

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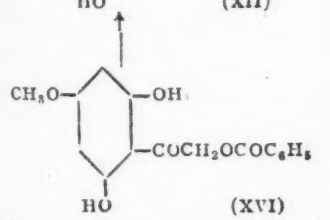

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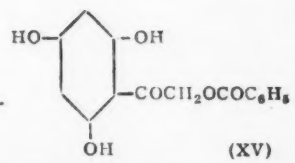
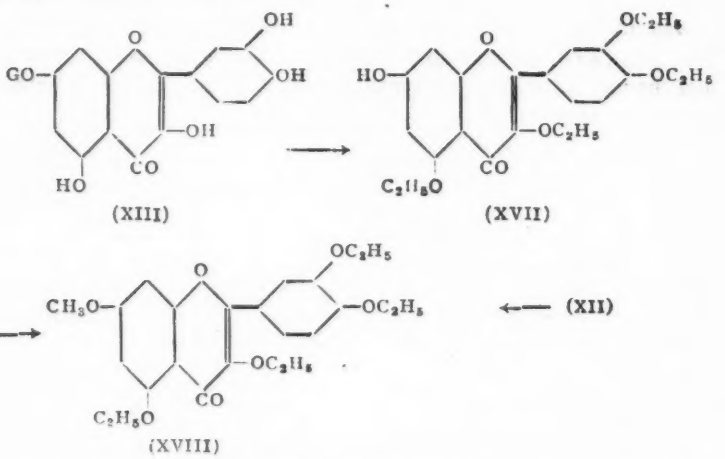


(XV)

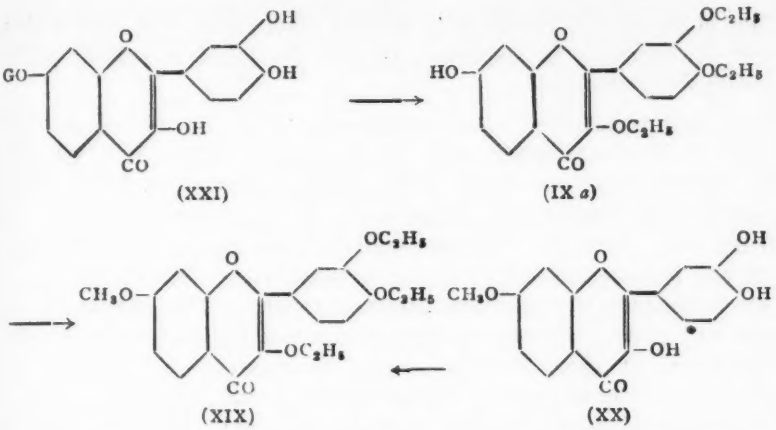
Synthetic confirmation of this constitution was lacking for over forty years. Only recently the synthesis of rhamnetin was reported by Kuhn, *et al.*[17] who started with ω-benzoyloxyphloracetophenone (XV). This was

methylated with diazomethane in methyl alcoholic solution whereby a poor yield of the 4-methyl ether (XVI) was obtained. Subsequent condensation with dibenzoyl protocatechuic anhydride in the presence of triethylamine as the condensing agent and hydrolysis of the benzoate yielded rhamnetin (XII).

An elegant method of showing the interrelationship between the above two quercetin derivatives is by ethylation. Quercimeritrin (XIII) obtained from the flowers of the combodia cotton plant is ethylated using excess of diethyl sulphate and anhydrous potassium carbonate in anhydrous acetone medium. The product is directly hydrolysed whereby the quercetin tetraethyl ether (XVII) is obtained melting at 200–201°. This resembles closely tetramethyl quercetin obtained similarly.[15] The melting point of the compound is high; it does not give any colour with ferric chloride and is soluble in alkali. Final methylation of it yields quercetin tetraethyl monomethyl ether (XVIII) melting at 118°. This is found to be identical with O-tetraethyl rhamnetin obtained by the direct ethylation of rhamnetin (XII). It should be mentioned here that for the ethylation of quercimeritrin, the use of diethyl sulphate is quite necessary whereas rhamnetin could be ethylated even by means of ethyl iodide.



A simpler compound useful for this type of work has also been synthesised now, namely 7-methoxy-3 : 3′ : 4′-triethoxy flavone (XIX). It will correlate the 7-methyl ether (XX) with the 7-glycoside of fisetin (XXI). The intermediate 7-hydroxy-3 : 3′ : 4′-triethoxy flavone (IX*a*) has already been mentioned.



The rhamnetin used for ethylation was kindly provided by Prof. L. H. Briggs of the University of New Zealand. It belonged originally to the preparations of Prof. A. G. Perkin. The rutin sample was kindly supplied by Dr. A. G. Clark of the Scripps Metabolic Clinic, La Jolla, San diego, California. For these gifts we are highly grateful.

Experimental

ω-Ethoxy-2: 4-dihydroxy-acetophenone.—A solution of dry resorcinol (8 g.) in anhydrous ether (75 c.c.) was treated with ethoxy acetonitrile[9] (6 c.c.) and freshly fused zinc chloride (2 g.). The mixture was cooled to 0° and saturated with dry hydrogen chloride during the course of an hour and a half. By this time a colourless precipitate of the ketimine hydrochloride had separated out. However the current of gas was continued for two hours more. The next morning the ether was decanted off and the ketimine hydrochloride washed thrice with anhydrous ether. It was hydrolysed by dissolving it in water (75 c.c.) and heating the solution at 80° for 30 minutes. On cooling a reddish brown liquid separated. It was extracted with ether and when the ether solution was evaporated a semi-solid residue was obtained. It was crystallised from hot water when the ketone was obtained in the form of stout elongated rectangular prisms and octagonal rods. Purification of the semi-solid ketone was also effected by distilling it under reduced pressure (10 mm.) when it passed over as a pale reddish brown oil between 195–200°; this solidified to a colourless crystalline solid almost immediately, m.p. 135–6°. Yield, 4 g. (Found: C, 61·0; H, 6·2; $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·1%).

The ketone was easily soluble in alcohol, ethyl acetate and acetone but sparingly in benzene. Its alcoholic solution developed a reddish violet colour with ferric chloride.

7-Hydroxy-3-ethoxy-3′: 4′-dimethoxy-flavone.—An intimate mixture of ω-ethoxy-2: 4-dihydroxy-acetophenone (1 g.), veratric anhydride (5 g.) and sodium veratrate (3 g.) was heated under reduced pressure at 170-80° for three hours. The product was refluxed with 10% alcoholic potash (80 c.c.) for 20 minutes. After the removal of alcohol, the residue was dissolved in water and the solution saturated with carbon dioxide. The flavone separated out in the form of a flocculent brown precipitate. This was repeatedly extracted with ether. The ether extract gave a pale yellow crystalline solid on evaporation. It crystallised from alcohol (charcoal) in the form of straw coloured elongated rectangular plates and needles melting at 194–5°. Yield, 0·6 g. (Found: C, 67·0; H, 5·0; $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3%.) It developed a bright purplish red colour in alcoholic solution on reduction with magnesium and hydrochloric acid. Its solution in concentrated sulphuric acid was bright yellow with no fluorescence. It gave no colour with alcoholic ferric chloride.

3-Ethoxy-7: 3′: 4′-trimethoxy-flavone (I).—The above flavone (0·2 g.) was dissolved in dry acetone (50 c.c.) and dimethyl sulphate (0·2 c.c.) and anhydrous potassium carbonate (1 g.) added. The mixture was refluxed for six hours. The solvent was then distilled off and the residue treated with water. The methyl ether separated out as a colourless crystalline solid. It crystallised from alcohol in the form of colourless rectangular prisms melting at 125–7°. (Found: C, 67·1; H, 5·5; $C_{20}H_{20}O_6$ requires C, 67·4; and H, 5·6%.)

7-Hydroxy-3: 3′: 4′-triethoxy-flavone (IX a).—ω-Ethoxy-2: 4-dihydroxy acetophenone (0·6 g.) was condensed as in a previous experiment with diethyl protocatechuic anhydride (4 g.) and sodium diethyl protocatechuate (2·5 g.). After hydrolysis of the condensation product, the alkali solution was saturated with carbon dioxide and the precipitated flavone separated by ether extraction. It recrystallised from alcohol in the form of pale yellow aggregates of rectangular plates melting at 192–3°. Yield, 0·9 g. (Found: C, 68·4; H, 6·3; $C_{21}H_{22}O_6$ requires C, 68·1; and H, 6·0%). When reduced with magnesium and hydrochloric acid in alcoholic solution, it developed a scarlet red colour. It dissolved in concentrated sulphuric acid yielding a bright yellow solution with no fluorescence. No colour developed with alcoholic ferric chloride.

3: 7: 3′: 4′-Tetraethoxy-flavone: Fisetin tetraethyl ether (IX).—A solution of the triethoxy-hydroxy flavone (0·5 g.) in anhydrous acetone (50 c.c.)

was refluxed with diethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (1 g.) for 12 hours. The solvent was then removed by evaporation and water added to the residue. The tetraethyl ether was filtered, washed and crystallised from alcohol. After two crystallisations it was obtained as colourless shining needles melting at 106–7° (*cf.* Perkin and Everest[18]). (Found: C, 69·0; H, 6·2; $C_{23}H_{28}O_6$ requires C, 69·3 and H, 6·5%.) It was soluble in concentrated sulphuric acid yielding a bright yellow solution with feeble green fluorescence. With magnesium and hydrochloric acid, it rapidly developed a bright orange colour.

7-*Methoxy*-3 : 3′ : 4′-*triethoxy-flavone* (*XIX*).—7-Hydroxy-3 : 3′ : 4′-triethoxy-flavone (0·2 g.) was refluxed for 8 hours with dimethyl sulphate (0·3 c.c.) and anhydrous potassium carbonate (1 g.) in dry acetone solution (50 c.c.). The methyl ether was precipitated as a colourless product when water was added to the residue after the removal of acetone. It crystallised from aqueous alcohol as colourless thin rectangular plates melting at 131–2°. (Found: C, 68·6; H, 6·0; $C_{22}H_{24}O_6$ requires C, 68·7; H, 6·3%.)

3-*Ethoxy*-5 : 7-*dihydroxy*-4′-*methoxy-flavone*.—This was obtained by heating ω-ethoxy phloroacetophenone (0·6 g.) with anisic anhydride (4·5 g.) and sodium anisate (3 g.) at 170–80° for three hours under reduced pressure. The condensation product was hydrolysed as in the previous cases and the flavone obtained by extraction with ether after saturating the alkali solution with carbon dioxide. It was crystallised from alcohol when it was obtained as bright yellow stout rectangular prisms and tablets melting at 194–6°. Yield, 0·8 g. (Found: C, 66·2; H, 4·8; $C_{18}H_{16}O_6$ requires C, 65·8 and H, 4·9%.) It dissolved in concentrated sulphuric acid yielding a bright yellow solution with green fluorescence. With neutral ferric chloride in alcohol, it developed a brow colour and with magnesium and hydrochloric acid, a pinkish red colour.

3-*Ethoxy*-5 : 7 : 4′-*trimethoxy-flavone* (*II*).—Methylation of the above flavone (0·5 g.) was carried out by refluxing it in acetone solution with dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (2 g.) for 20 hours. The product was worked up as in previous cases. The methyl ether crystallised from alcohol in the form of colourless elongated rectangular prisms and rods melting at 102–3°. (Found: C, 67·2; H, 5·5; $C_{20}H_{20}O_6$ requires C, 67·4; H, 5·6%.)

Its solution in concentrated sulphuric acid was bright yellow exhibiting strong green fluorescence. A bright red colour was obtained when it was reduced in alcoholic solution with magnesium and hydrochloric acid.

3-*Ethoxy*-5 : 7-*dihydroxy*-3′ : 4′-*dimethoxy-flavone*.—Condensation of ω-ethoxy phloroacetophenone (1 g.) with veratric anhydride (8 g.) and sodium veratrate (2 g.) was effected as in previous cases by heating the mixture under

reduced pressure for three hours at 170-80° and the condensation product worked up. The flavone crystallised from alcohol in the form of very pale yellow short needles melting at 189–90°. Yield, 0·9 g. (Found: C, 64·0; H, 5·0; $C_{19}H_{18}O_7$ requires C, 63·7 and H, 5·0%.) It gave a bright yellow solution with concentrated sulphuric acid with feeble green fluorescence. With ferric chloride in alcoholic solution, it yielded a reddish brown colour and with magnesium and hydrochloric acid, an orange red colour.

3-*Ethoxy*-5: 7: 3′: 4′-*tetramethoxy-flavone* (*III*).—Methylation of the above flavone (0·3 g.) was effected with dimethyl sulphate (0·2 c.c.) and anhydrous potassium carbonate (1 g.) in dry acetone solution (50 c.c.). After refluxing for six hours, the solvent was distilled off and water added. The colourless precipitate was filtered and crystallised from alcohol when it was obtained as colourless narrow rectangular needles and plates melting at 154–5°. (Found: C, 65·0; H, 6·0; $C_{21}H_{22}O_7$ requires C, 65·3 and H, 5·7%.)

ω-Ethoxy-4: 6-*dimethoxy*-2-*hydroxy-acetophenone* (*VII*).—(*a*) ω-Ethoxyphloroacetophenone (1 g.; 1 mol.) was treated in anhydrous acetone solution (50 c.c.) with dimethyl sulphate (1 c.c.; 2·2 mol.) and anhydrous potassium carbonate (5 g.) and the mixture refluxed for 12 hours. The solvent was then distilled off, water added and the solid product filtered off. It was macerated with 5% aqueous potash (25 c.c.) and filtered. The filtrate on acidification yielded the colourless dimethyl ether which crystallised from aqueous alcohol in the form of colourless rectangular prisms melting at 103–4°. Yield, 0·7 g. (Found: C, 59·9; H, 7·0; $C_{12}H_{16}O_5$ requires C, 60·0; and H. 6·7%.)

(*b*) 3-Ethoxy-5: 7: 3′: 4′-tetramethoxy flavone (III) (0·5 g.) was refluxed with 8% absolute alcoholic potash (25 c.c.) for four hours. At the end of this period the solvent was distilled off and water added to the residue. The alkaline solution was then saturated with carbon dioxide and extracted with ether several times. On removing the ether from the extract a colourless crystalline solid was obtained. It was recrystallised from aqueous alcohol using animal charcoal. The ketone was thus obtained in the form of colourless rectangular prisms melting at 103–4°. A mixed melting point with the sample obtained in (*a*) above was not depressed.

Methylation of Rutin.—Rutin (1 g.) was refluxed in acetone solution (150 c.c.) with dimethyl sulphate (4 c.c.) and anhydrous potassium carbonate (10 g.) for 45 hours. The acetone was then distilled off and water added to the residue. The resulting colourless precipitate was used directly for the next experiment.

3-*Hydroxy*-5: 7: 3′: 4′-*tetramethoxy flavone* (*VI*).—The above precipitate was hydrolysed by refluxing for one and a half hours with 7% aqueous-alcoholic sulphuric acid (30 c.c.). The alcohol was then distilled off and

more water added. A bright yellow precipitate was obtained. It was filtered and crystallised from alcohol when it came out in the form of bright yellow elongated needles and prisms. It melted at 197-8° (*cf.* Kostanecki and Tambor[14]).

3-*Ethoxy*-5: 7: 3′: 4′-*tetramethoxy flavone* (*III*).—The above hydroxy flavone (0·5 g.) was refluxed for six hours in anhydrous acetone solution (50 c.c.) with diethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (2 g.). The acetone was then distilled off and water added to the residue. A colourless crystalline precipitate was obtained which when recrystallised from alcohol was obtained as colourless narrow rectangular needles and plates melting at 154–5°. A mixed melting point with a synthetic sample was not depressed.

Ethylation of quercimeritrin and hydrolysis of the ethyl ether.—Dried and finely powdered quercimeritrin (1 g.) was suspended in anhydrous acetone (75 c.c.) and treated with anhydrous potassium carbonate (10 g.) and diethyl sulphate (4·5 c.c. added in three lots). The mixture was refluxed for a period of 40 hours. It was then filtered and the potassium salts washed thrice with hot acetone. The acetone filtrate and washings were evaporated when a semi-solid mass was obtained. This was directly hydrolysed by refluxing with 7% aqueous alcoholic sulphuric acid (75 c.c.) for two hours. The alcohol was then evaporated off. The tetraethyl quercetin (XVII) that separated was filtered and crystallised from alcohol when it was obtained in the form of pale yellow stout rhombic prisms melting at 200–201°. Yield, 0·6 g. It dissolved readily in aqueous alkali yielding a pale yellow solution and gave no colour with ferric chloride. (Found: C, 66·3; H, 6·6; $C_{23}H_{23}O_7$ requires C, 66·7; and H, 6·3%.)

7-*Methoxy*-3: 5: 3′: 4′-*tetraethoxy-flavone* (*XVIII*).—The foregoing O-tetraethyl-quercetin (0·2 g.) was methylated by means of dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (2 g.) in dry acetone medium. After refluxing for 8 hours the contents were filtered and the potassium salts washed with hot acetone. The filtrate and the washings were evaporated to dryness. The colourless crystalline solid obtained was recrystallised from aqueous alcohol when the methyl ether came out as colourless aggregates of thin micacious plates melting at 119–20°. The melting point was not depressed on admixture with O-tetra-ethyl-rhamnetin given below. (Found: C, 67·0; H, 6·7; $C_{24}H_{23}O_7$ requires C, 67·3 and H, 6·5%.)

O-Tetra-ethyl-rhamnetin.—Rhamnetin (0·2 g.) was ethylated by refluxing in acetone solution with diethyl sulphate (1·5 c.c. added in 3 lots) and anhydrous potassium carbonate (5 g.) for 36 hours. The acetone was then distilled off and water added to the residue. A colourless solid separated

out. It was filtered and crystallised from aqueous alcohol when it wa obtained in the form of colourless stout rectangular prisms melting at 119–20°. The mixed melting point with 7-methoxy-3 : 5 : 3′ : 4′-tetraethoxy-flavone (XVIII) obtained from quercimeritrin was not depressed.

Summary

The use of ethylation in the study of naturally occurring glycosides and partial methyl ethers of hydroxy flavones is discussed. This procedure renders the work simpler and more definite. Starting from ω-ethoxy res- and phloracetophenones, the preparation of mixed ethyl methyl ethers of the flavonols, fisetin, kæmpferol, and quercetin, with an ethoxyl in the 3-position and methoxyls in the other positions, is described and it is shown that these compounds are useful in the study of the 3-glycosides of these flavonols. The case of rutin has been used as a typical example.

As an illustration of the synthesis of fully ethylated compounds fisetin tetraethyl ether is made and as an example for the use of ethylation in the study of both 7- glycosides and 7- methyl ethers, O-3 : 3′ : 4′-triethyl-7-methyl-fisetin is synthesised.

The use of ethylation for establishing interrelationship between glycosides and partial methyl ethers of hydroxy flavones is illustrated with the case of quercimeritrin and rhamnetin. Quercimeritrin has been ethylated with diethyl sulphate and the ethylated glucoside hydrolysed and methylated. The product is a mixed ether of quercetin and is shown to be identical with O-tetraethyl rhamnetin.

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THE SCALAR INVARIANTS OF A GENERAL GRAVITATIONAL METRIC

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1. Introduction

The absolute scalar invariants of order two associated with the four-dimensional Riemannian metric,

$$ds^2 = g_{\mu\nu}\, dx^\mu\, dx^\nu, \tag{1}$$

which is used in the general theory of relativity, have a special significance as the field equations are partial differential equations of second order. The metric tensor $g_{\mu\nu}$ and the Riemann-Christoffel curvature tensor R_{hijk} have ten and twenty independent components respectively. At the same time it can be shown that there are only sixteen independent differential equations for the determination of these scalar invariants. Thus one finds that there are only fourteen[1] (*i.e.*, $10+20-16$) independent scalar invariants of the second order.

So far as we know, no attempt has been made to obtain a set of fourteen independent scalar invariants. It is the object of this paper to present such a set. We find it convenient in the present investigation to set up two tensors, R_{ij} and C_{hijk}, each representing ten linear combinations of R_{hijk}-components, so that a necessary and sufficient condition for

$$R_{hijk} = 0 \tag{2}$$

is that both

$$\text{(i) } R_{ij} = 0, \text{ (ii) } C_{hijk} = 0. \tag{3}$$

We have

$$R_{ij} = g^{hk} R_{hijk}, \tag{4}$$

and as the only linear combinations of R_{hijk}-components which preserve all the symmetry properties are

$$\text{(i)}\ a(g_{hj}g_{ik}-g_{hk}g_{ij})R, \tag{5}$$

$$\text{(ii)}\ b(g_{hj}R_{ik}+g_{ik}R_{hj}-g_{hk}R_{ij}-g_{ij}R_{hk}), \tag{6}$$

we consider

$$C_{hijk}=R_{hijk}+a(g_{hj}g_{ik}-g_{hk}g_{ij}) + b(g_{hj}R_{ik}+g_{ik}R_{hj}-g_{hk}R_{ij}-g_{ij}R_{hk}), \tag{7}$$

a and b being unknown scalars. The condition

$$g^{hk}C_{hijk}=0 \tag{8}$$

implies, for n dimensions,

$$1+2b-bn=0,\ a(n-1)+b=0, \tag{9}$$

which means that the tensor C_{hijk} is Weyl's conformal curvature tensor, having only ten independent components for $n=4$. Weyl's projective tensor is apparently simpler but it has not the same symmetry properties and we do not find it as useful as the conformal curvature tensor in our work.

2. A Set of Fourteen Scalar Invariants

The fourteen invariants and the various tensors associated with them are defined as follows:—

$$\left.\begin{aligned}
A_{hijk}&=C_{hipq}C_{rsjk}g^{pr}g^{qs}\\
B_{hijk}&=C_{hipq}A_{rsjk}g^{pr}g^{qs}\\
D_{hijk}&=B_{hijk}-\tfrac{1}{12}J_2(g_{hj}g_{ik}-g_{hk}g_{ij})-\tfrac{1}{4}J_1C_{hijk}\\
\overline{D}_{hijk}&=(J_3)^{-\frac{1}{3}}\cdot D_{hijk}\\
E_{hijk}&=C_{hipq}D_{rsjk}g^{pr}g^{qs}\\
F_{hijk}&=C_{hipk}E_{rsjk}g^{pr}g^{qs}
\end{aligned}\right\} \tag{10}$$

$$Q_\gamma{}^\mu=R_\alpha{}^\mu R_\gamma{}^\alpha; \tag{11}$$

$$I_1=R_\mu{}^\mu,\ I_2=R_\alpha{}^\mu R_\mu{}^\alpha,\ I_3=R_\alpha{}^\mu R_\beta{}^\alpha R_\mu{}^\beta, \qquad I_4=R_\alpha{}^\mu R_\beta{}^\alpha R_\delta{}^\beta R_\mu{}^\delta; \tag{12}$$

$$J_1 = A_{hijk} g^{hj} g^{ik},\ J_2 = B_{hijk} g^{hj} g^{ik},$$

$$J_3 = E_{hijk} g^{hj} g^{ik},\ J_4 = F_{hijk} g^{hj} g^{ik}; \tag{13}$$

$$K_1 = C_{hijk} R^{hj} R^{ik},\ K_2 = A_{hijk} R^{hj} R^{ik},\ K_3 = \overline{D}_{hijk} R^{hj} R^{ik}$$

$$K_4 = C_{hijk} Q^{hj} Q^{ik},\ K_5 = A_{hijk} Q^{hj} Q^{ik},\ K_3 = D_{hijk} Q^{hj} Q^{ik}. \tag{14}$$

One of us has verified by direct calculation that the fourteen invariants defined by (12), (13) and (14) are independent in the algebraic sense. The actual computation was simplified by neglecting the cross terms of $g_{\mu\gamma}$ and $R_{\mu\gamma}$ and it was found that the reduced expressions of the fourteen invariants were functions of fourteen independent variables, the Jacobian being non-zero.

3. Gravitational Interpretations

The vanishing of the fourteen invariants does not imply the vanishing of R_{hijk}. We give later an example of a non-flat metric for which all the invariants vanish.

We start our discussion with a class of metrics for which the number of non-zero R_{hijk}-components is essentially six, the number of independent scalar invariants also being six. This enables us to obtain a number of interesting results bringing out the importance of the invariants.

We proceed to consider a line-element

$$ds^2 = g_{11}(dx^1)^2 + g_{22}(dx^2)^2 + g_{33}(dx^3)^2 + g_{44}(dx^4)^2, \tag{15}$$

which has the additional property that

$$R_{1212},\ R_{1313},\ R_{1414},\ R_{2323},\ R_{2424},\ R_{3434} \tag{16}$$

constitute a complete set of independent and surviving components of R_{hijk}. The line-element for example,

$$ds^2 = \bar{g}_{11}(dx^1)^2 + \bar{g}_{22}(dx^2)^2 + \bar{g}_{33}(dx^3)^2 + (dx^4)^2, \tag{17}$$

where $\bar{g}_{11}$, $\bar{g}_{22}$, $\bar{g}_{33}$ are functions of x^4 only, is found to satisfy (15) and (16). A general spherically symmetrical line-element, which is of considerable importance in the general theory of relativity, is given by

$$ds^2 = -A dr^2 - B(d\theta^2 + \sin^2\theta d\phi^2) + 2C dr dt + D dt^2, \tag{18}$$

A, B, C, D being functions of r and t. The surviving components of R_{hijk} are given by

$$R_{1313} = R_{1212} \sin^2\theta,\ R_{1414},\ R_{2323},$$

$$R_{3434} = R_{2424} \sin^2\theta,\ R_{3143} = R_{2142} \sin^2\theta. \tag{19}$$

By a suitable transformation of co-ordinates

$$\bar{r} = \bar{r}(r, t),\ \bar{t} = \bar{t}(r, t),\ \bar{\theta} = \theta,\ \bar{\phi} = \phi, \tag{20}$$

(18) can be reduced to the form,

$$ds^2 = -\bar{A}(d\bar{r})^2 - \bar{B}(d\bar{\theta}^2 + \sin^2\bar{\theta}\, d\bar{\phi}^2) + D d\bar{t}^2, \tag{21}$$

so that the only surviving components of $\bar{R}_{hijk}$ are

$$\bar{R}_{1313} = \bar{R}_{1212} \sin^2\bar{\theta},\ \bar{R}_{3434} = \bar{R}_{2424} \sin^2\bar{\theta},\ \bar{R}_{1414},\ \bar{R}_{2323}. \tag{22}$$

Thus a general spherically symmetrical line-element is also reducible to the form (15) complying with (16). We, therefore, discuss the line-element (15) in detail. Only two of the independent components of C_{hijk} are non-zero while only four of the R_{ij}-components survive. It is obvious that the six invariants

$$I_1,\ I_2,\ I_3,\ I_4,\ J_1,\ J_2 \tag{23}$$

of which the first four are exclusively functions of R_{ij} and the last two are exclusively functions of the two independent components of C_{hijk}, are algebraically independent. It follows that if R_{hijk} vanishes all the six vanish and that the converse of this also holds. Again if C_{hijk} is zero, J_1 and J_2 also vanish and conversely the vanishing of J_1 and J_2 implies that of C_{hijk}. Let us consider what happens if (15) represents a space of constant curvature K_0, the necessary and sufficient conditions for this being

$$R_{hijk} = K_0 (g_{hj} g_{ik} - g_{hk} g_{ij}). \tag{24}$$

On using (24) we get

$$I_1 = 4(-3K_0),\ I_2 = 4(-3K_0)^2,\ J_1 = 0,$$

$$I_3 = 4(-3K_0)^3,\ I_4 = 4(-3K_0)^4,\ J_2 = 0. \tag{25}$$

Conversely, if (25) is satisfied, we can show that

$$R_1^1 = R_2^2 = R_3^3 = R_4^4 = -3K_0,\ R_\nu^\mu = 0\ (\mu \neq \nu),\ C_{hijk} = 0 \qquad (26)$$

On expressing these in terms of R_{hijk}, we find that these imply (24). Thus for the special line-element under consideration the necessary and sufficient conditions that the line-element may represent (1) a flat space, (ii) a Riemannian space of constant curvature, can be expressed in terms of these invariants. All these results are true for a general spherically symmetrical line-element which has been shown to be a particular case of the line-element under consideration. In addition, we find that due to the relations (22) there are only four independent scalar invariants associated with a general spherically symmetrical line-element and may be supposed to be given by I_1, I_2, I_3 and J_1. Incidentally it may be noted that the tensor D_{hijk} vanishes for the line-element (15) satisfying (16).

We return to the discussion of the general line-element (1). It is obvious that if R_{hijk} vanishes all the invariants must vanish. Since there are twenty independent components of R_{hijk} while there are only fourteen independent invariants R_{hijk} may not vanish even if all the invariants are zero. As an example, let us consider the line-element,

$$ds^2 = -A(\xi)\,[(dx^1)^2 + (dx^2)^2 + (dx^3)^2 - (dx^4)^2] \qquad (27)$$

$$\xi \equiv (x^1 - x^4).$$

It is conformal to a Euclidian metric and C_{hijk} is zero. Therefore the only possible non-vanishing invariants are I_1, I_2, I_3, I_4. The surviving components of R_j^i are given by

$$R_1^1 = R_1^4 = -R_4^1 = -R_4^4 = \frac{1}{A^2}\frac{d^2A}{d\xi^2} - \frac{3}{2}\cdot\frac{1}{A^3}\left(\frac{dA}{d\xi}\right)^2. \qquad (28)$$

It easily follows that I_1, I_2, I_3, I_4 are all zero. Thus (27) is an example of a non-flat line-element for which *all the scalar invariants of the second order vanish*. It represents the gravitational field caused by radiation flowing in the x^1-direction. Tolman[2] has given a first order solution of the problem. As far as we know no such line-element possessing this striking geometrical property has been discovered before.

From the set we have obtained it follows that if R_{ij} is not zero but all the fourteen invariants vanish there are ten restrictions on the ten independent components of C_{hijk} and hence C_{hijk} must vanish. Thus the metric is necessarily conformal to a flat space metric. Alternatively, if R_{ij} vanishes and the invariants also vanish it virtually amounts to only four restrictions on the ten C_{hijk}-components and hence C_{hijk} need not be zero. A result similar to this can be established for a general n-dimensional Riemannian space.

It is well known that a necessary condition that a Riemannian space be of class one[3] is

$$R_{hijk} = \pm (b_{hj} b_{ik} - b_{hk} b_{ij}), \tag{29}$$

b_{ij} being a symmetrical tensor. For the four-dimensional metric (1), R_{hijk} and b_{ij} have respectively twenty and ten independent components and by the elimination of b_{ij} we can get ten conditions to be satisfied by the R_{hijk}-components. It can be shown that there are only four independent invariants associated with b_{ij}, by the argument used to esbtalish the existence of fourteen independent scalars associated with R_{hijk}. If a line-element is of class one the fourteen invariants would be functions of only four invariants associated with b_{ij}. Hence, by elimination, the necessary condition (29) can be expressed as a set of ten relations between the fourteen invariants. In the case of a general spherically symmetrical line-element the conditions (29) reduce to one[4] which is also found to be sufficient that it may be of class one. Thus for a general spherically symmetrical line-element a necessary and sufficient condition that it may be of class one can be expressed in terms of scalar invariants. A result similar to the one obtained above can be shown to hold good for a general n-dimensional Riemannian space of class one.

SUMMARY

A set of fourteen independent scalar invariants of the second order, associated with a general four-dimensional Riemannian metric, is obtained. The set is found to reduce only to four independent invariants in the case of a general spherically symmetrical line-element. Moreover it is shown that the necessary and sufficient conditions that a general spherically symmetrical line-element may represent (i) a flat space, (ii) a Riemannian space of constant curvature, (iii) a Riemannian space conformal to a flat space,

(iv) a Riemannian space of class one, can be expressed in terms of these invariants. A new line-element which is the first of its kind known to us is also given, representing the gravitational field due to radiation flowing in one direction and for which all the scalar invariants of the second order vanish.

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PRODUCTION OF THE *JOSHI-EFFECT* IN Br_2 AND H_2 AND THEIR MIXTURES

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Discovered originally in chlorine as an instantaneous and reversible variation, usually though not invariably, a diminution in the discharge current when the gas is subjected to silent electric discharge in a Siemens' ozonizer, the *Joshi-Effect* is found as a result of extensive work in these laboratories to occur also in a number of other gases, both elemental and compound, and their mixtures, *e.g.*, Br_2, I_2, air, N_2, O_2, S, Se, NO_2, HCl and metallic vapours such as Hg, K and Na.[7, 8, 12, 13] Detailed investigations of Deo and others on chlorine have shown that, under optimum conditions of various factors such as applied potential, pressure of the gas, intensity and frequency of the illumination, etc., which control and determine the magnitude and even the sign of the *Joshi-Effect*, chlorine can give as high as 93–98% negative *Joshi-Effect*.[10] Subsequent detailed work on other systems has brought to light the fact that the *Joshi-Effect* is a widely-occurrent phenomenon and is exhibited by numerous gases and vapours and that its magnitude can be made as large as in chlorine by an appropriate manipulation of the relevant parameters.

In the case of bromine, it was thought at first that the magnitude of the *Joshi-Effect* was very much smaller than in chlorine. Deshmukh[1] could not find more than about 7% *Joshi-Effect* in Br_2 while the *Effect* in H_2 was negligible. Since extensive and detailed work subsequently carried out in these laboratories has revealed both positive and negative *Joshi-Effect* of large magnitudes in other systems such as elemental gases and especially their mixtures, it appeared desirable to re-study the systems Br_2 and H_2 and their mixtures. Also, since Joshi's theory[5, 6] for the phenomenon contemplates the 'electron affinity' of the excited medium as a primary determinant of the associated negative *Effect*, it was of interest to investigate the phenomenon in Br_2 admixed with a gas like H_2 with a comparatively low electron affinity; and with Cl_2 whose electron affinity is more pronounced. The present investigations, as expected, have brought to light the occurrence of

large negative *Joshi-Effect* in these systems. What is more remarkable is the fact that Br_2, a strongly electronegative gas, shows the positive *Joshi-Effect* as well, while H_2, which in the fresh condition gives the negative *Effect* only, undergoes a striking change in its behaviour when 'aged' under the discharge and gives increasingly large positive *Joshi-Effect*. It may be mentioned that this constitutes the first instance of the observation of positive *Joshi-Effect* in Br_2.

Experimental

The general set up of the apparatus and experimental technique are essentially the same as described in the author's previous paper.[12] The purified gases, Cl_2, Br_2, H_2 and their mixtures, were admitted into the reaction vessel of the type of an all-glass Siemens' ozonizer at the required pressures read by a glass spoon manometer of the type used by Jackson[2] and exposed to the required applied potential obtained from a step-up transformer fed by single phase alternating current of 500 cycles frequency. A system of two 200-watt electric bulbs mounted suitably could irradiate the ozonizer transversely. The ozonizer itself was enclosed in a box provided with a shutter by which arrangement the ozonizer could be irradiated or shielded from light as required. The discharge current was measured by means of a double wave rectifier type Cambridge microammeter.

Table I (*a–h*) contains some typical data for the *Joshi-Effect*, calculated as Δi, the net *Effect* (*i.e.*, $i_L - i_D$) and $\%\Delta i$ (*i.e.*, $100(i_L - i_D)/i_D$ in pure Br_2 and in Br_2, Cl_2 mixtures. The partial pressure of Br_2 was kept constant at 47 mm. while that of Cl_2 was varied in the range 28–257 mm. The variation in the magnitude of the *Effect* with the applied potential, for a particular pressure of the gas, was observed by gradually increasing the applied potential from values less than V_m, the threshold potential of the system to values well above V_m. The data for the potential variation of the *Joshi-*

Table I

Potential Variation of Joshi-Effect *in Br_2 and in Br_2, Cl_2 mixtures*

(*a*) Pressure of Br_2 = 47 mm.

kV	i_D	i_L	Δi	$\%\Delta i$
0·40	7·0	10·0	+3·0	+42·9
0·53	13·0	13·0	0	0
0·67	20·0	20·0	0	0
0·80	30·0	29·0	−1·0	−3·3
0·93	40·0	38·5	−1·5	−3·75

(*b*) Pressure of Br_2 = 47 mm.
,, Cl_2 = 28 mm.

kV	i_D	i_L	Δi	$\%\Delta i$
0·40	−1·0	−1·0	0	0
0·67	3·75	0	− 3·75	−100
0·80	25·5	17·0	− 8·5	−31·3
0·93	56·5	43·0	−13·5	−23·9

TABLE I—(*Contd.*)

(*c*) Pressure of Br_2 = 47 mm.
,, Cl_2 = 62 mm.

kV	i_D	i_L	Δi	$\%\Delta i$
0·40	−1·0	−1·0	0	0
0·67	−1·5	−1·5	0	0
0·80	5·5	0·25	− 5·25	−95·5
0·93	22·5	13·5	− 9·0	−40·0
1·07	46·0	34·0	−12·0	−26·1
1·20	79·0	66·0	−13·0	−16·5

(*d*) Pressure of Br_2 = 47 mm.
,, Cl_2 = 96 mm.

kV	i_D	i_L	Δi	$\%\Delta i$
0·67	−1·5	−1·5	0	0
0·80	−1·75	−2·25	− 0·75	− 42·9
0·93	3·5	−1·0	− 4·5	−128·6
1·07	13·0	7·0	− 6·0	− 46·2
1·20	31·0	21·0	−10·0	− 32·3
1·33	52·0	39·0	−13·0	− 25·0
1·47	78·0	68·0	−10·0	− 12·8

(*e*) Pressure of Br_2 = 47 mm.
,, Cl_2 = 131 mm.

kV	i_D	i_L	Δi	$\%\Delta i$
0·67	−1·0	−1·0	0	0
0·80	−1·5	−1·5	0	0
0·93	−2·0	−2·25	− 0·25	− 12·5
1·07	0	−3·0	− 3·0	− ∞
1·20	5·5	−1·5	− 7·0	−127·3
1·33	13·0	5·0	− 8·0	− 61·5
1·47	26·5	17·0	− 9·5	− 35·8
1·60	46 0	36·0	−10·0	− 21·7
1·73	73·0	62·0	−11·0	− 15·1

(*f*) Pressure of Br_2 = 47 mm.
,, Cl_2 = 206 mm.

kV	i_D	i_L	Δi	$\%\Delta i$
0·67	−1·0	−1·0	0	0
0·80	−2·0	−2·0	0	0
0·93	−2·5	−2·5	0	0
1·07	−3·5	−3·5	0	0
1·20	−3·5	−4·0	− 0·5	− 14·4
1·33	−3·5	−5·0	− 1·5	− 42·9
1·47	−1·0	−5·5	− 4·5	−450
1·60	4·5	−3·0	− 7·5	−167
1·73	10·75	1·0	− 9·75	−90·8
1·87	22·0	10·0	−12·0	−54·5
2·00	38·0	26·0	−12·0	−31·6

(*g*) Pressure of Br_2 = 47 mm.
,, Cl_2 = 234 mm.

kV	i_D	i_L	Δi	$\%\Delta i$
0·67	−1·25	−1·25	0	0
0 80	−1·5	−1·5	0	0
0·93	−2·25	−2·25	0	0
1·07	−2·75	−2·75	0	0
1·20	−3·25	−3·5	− 0·25	− 7·7
1·33	−2·5	−4·5	− 2·0	−80·0
1·47	−1·0	−5·0	− 4·0	−400
1·60	3·5	−4·5	− 8·0	−229
1·73	9·0	−1·5	−10·5	−117
1·87	21·0	8·0	−11·0	−62·0
2·00	40·0	25·0	−15·0	−37·5
2·13	67·0	50·0	−29·0	−43·3

(*h*) Pressure of Br_2 = 47 mm.
,, Cl^2 = 257 mm.

kV	i_D	i_L	Δi	$\%\Delta i$
0·67	−1·0	−1·0	0	0
0·80	−1·25	−1·25	0	0
0·93	−2·0	−2·0	0	0
1·07	−2·25	−2·25	0	0
1·20	−3·0	−3·0	0	0
1·33	−3·25	−3·75	− 0·25	− 7·7
1·47	−2·25	−4·75	− 2·5	− 111
1·60	−0·25	−5·0	− 4·75	−1900
1·73	2·5	−4·5	− 7·0	− 280
1·87	7·0	−2·25	− 9·25	− 132
2·00	16·25	4·0	−12·25	−75·4
2·13	33·0	18·5	−14·5	−43·9
2·27	57·0	40·5	−16·5	−28·9
2·40	78·0	62·0	−16·0	−20·5

Effect in pure H_2 taken at 252 mm. are given in Table II while in Table III are returned similar data for Br_2, H_2 mixtures. Table IV summarises the behaviour of H_2 with regard to the production of the *Joshi-Effect*, when the gas is sealed off in the ozonizer at 50 mm. and ' aged ' for different periods at 0.40 kV.

TABLE II

Potential variation of Joshi-Effect *in* H_2

Pressure of H_2 = 252 mm

kV	i_D	i_L	Δi	$\%\Delta i$
0·40	−1·0	−1·0	0	0
0·43	−1·5	−1·5	0	0
0·45	−1·5	4·5	+6·0	+400
0·48	30·5	30·5	+0·5	+1·7
0·51	43·0	43·0	0	0
0·53	58·0	58·0	0	0
0·56	72·0	72·0	0	0

TABLE III

Potential variation of Joshi-Effect *in* H_2, Br_2 *mixtures*

(*a*) Pressure of Br_2 = 72 mm.
,, H_2 = 92 mm.

kV	i_D	i_L	Δi	$\%\Delta i$
0·67	−0·75	−0·5	+ 0·25	+33·3
0·80	13·0	8·0	− 5·0	−38·5
0·93	38·0	27·0	−11·0	−29·0
1·07	62·0	48·0	−14·0	−22·6

(*b*) Pressure of Br_2 = 72 mm.
,, H_2 = 173 mm.

kV	i_D	i_L	Δi	$\%\Delta i$
0·67	−1·25	−0·5	+ 0·75	+60·0
0·80	0·5	2·75	+ 2·25	+450
0·93	12·5	12·5	0	0
1·07	36·0	28·0	− 8·0	−22·2
1·20	60·0	50·0	−10·0	−16·7

TABLE IV

Influence of ' ageing ' on the potential variation of Joshi-Effect

(*a*) Pressure of H_2 = 50 mm.
(The gas was freshly introduced into the ozonizer and sealed)

kV	i_D	i_L	Δi	$\%\Delta i$
0·27	23·5	23·5	0	0
0·30	24·5	24·5	0	0
0·32	28·5	28·5	0	0
0·35	34·0	34·0	0	0
0·38	42·5	42·5	0	0
0·40	49·0	49·0	0	0

(*b*) After ' ageing ' the gas at 0·40 kV for 3 hours

kV	i_D	i_L	Δi	$\%\Delta i$
0·27	28·0	29·0	+1·0	+3·6
0·30	47·0	45·5	−1·5	−3·2
0·32	57·0	54·0	−3·0	−5·3
0·35	66·0	63·0	−3·0	−4·5

TABLE IV—(*Contd.*)

(*c*) After 'ageing' the gas at 0·40 kV for another 6 hours

kV	i_D	i_L	Δi	$\%\Delta i$
0·35	20·0	38·0	+18	+90
0·38	38·0	49·0	+11	+29
0·40	49·0	56·0	+ 7	+24·3
0·43	65·0	67·0	+ 2	+ 3·1

(*d*) After 'ageing' the gas at 0·40 kV for another 3 hours

kV	i_D	i_L	Δi	$\%\Delta i$
0·43	0	33·0	+33	+ ∞
0·45	4·0	36·0	+32	+800
0·48	13·0	42·0	+29	+223
0·51	30·0	49·0	+19	+63·3
0·53	49·0	60·0	+11	+22·5

(*e*) After 'ageing' the gas at 0·40 kV for another 11 hours

kV	i_D	i_L	Δi	$\%\Delta i$
0·43	0	37·0	+37	+∞
0·45	0	41·0	+41	+∞
0·48	1·0	46·0	+45	+4500
0·51	8·0	51·0	+43	+538
0·53	32·0	59·0	+27	+84·4
0·56	46·0	66·0	+20	+43·5

(*f*) After 'ageing' the gas at 0·40 kV for another 15 hours

kV	i_D	i_L	Δi	$\%\Delta i$
0·48	0	22·0	+22·0	+∞
0·51	0	26·5	+26·5	+∞
0·53	0	31·5	+31·5	+∞
0·56	0·5	37·5	+37·0	+7400
0·58	4·0	44·5	+40·5	+1013
0·61	4·5	48·0	+43·0	+967
0·64	5·0	52·0	+47·0	+940

DISCUSSION

It is seen from Table I (*a–h*) that while pure Br_2 at 47 mm. gives only about 4% negative *Joshi-Effect*, mixtures of Br_2 and Cl_2 give very large negative *Joshi-Effect*. In conformity with earlier findings in the case of Cl_2[9], $-\%\Delta i$, for a particular pressure of the gaseous mixture, rises (numerically) to a maximum and then falls as the applied potential is continuously increased. $-\Delta i$ also shows a similar *numerical* rise with the applied potential; but the subsequent fall in $-\Delta i$ noticed in Cl_2 is absent here probably because of the narrow range of the applied potential which could not be raised to higher values because of the limited range of the available current detector, *viz.*, the microammeter. The behaviour of pure Br_2 at 47 mm is striking in that it gives 43% positive *Joshi-Effect* at low potentials. This positive *Effect* decreases to zero as the applied potential is increased by a small amount. At higher potentials, the familiar negative *Effect* is obtained. When Cl_2 is admixed with Br_2, the positive *Effect* disappears completely. This has obvious significance for the mechanism of the positive *Effect* (*vide infra*). As the partial pressure of Cl_2 increases in the mixture, the V_m of the system, as is to be expected, increases and hence the *Joshi-Effect* develops at higher and higher potentials.

It may be noted that in the Tables given above, i_D and i_L are sometimes given the negative sign. This is an instance of the abnormal working of the oxide rectifier in the microammeter. It was observed that the microammeter behaved strangely especially at low applied potentials. The pointer of the microammeter which was at zero when no potential was applied, moved backwards at low potentials showing, as it were, a negative current. As the applied potential was increased, the pointer moved gradually to the right going back to zero at some particular potential and then to the right showing the normal positive current at higher potentials. This apparently anomalous behaviour of the microammeter is to be attributed to the limited performance of the copper oxide rectifier in responding to all the frequencies present in the discharge current. It is known as a result of Joshi's oscillographic studies of the structure of the discharge current[4] that the current consists in addition to the fundamental frequency of the A.C. supply and its harmonics, a large number of higher frequencies of varying strengths. The relative proportion of these frequencies presumably changes as the applied potential is varied. The copper oxide rectifier of the microammeter seems to show a preferential response to some of the frequencies present in the discharge current and so effects only a partial rectification. This may account for the instrument indicating a negative current at low potentials.

The demands of consistency in calculating the net *Joshi-Effect*, Δi by subtracting i_D from i_L made it necessary to take the sign of the current into account. This leads to the abnormally large values, as high as 1900%, for the negative *Joshi-Effect* which, when viewed simply as photo-suppression of the current, should not exceed 100%.

Another result which emerges out of an examination of Table I and which is in accord with earlier findings[9] is that at a given applied potential, $-\%\Delta i$ (numerically) increases to a maximum and then decreases as the gas pressure is continuously increased. The net *Joshi-Effect*, $-\Delta i$, however, shows no such approach to a limiting condition but a progressive decrease with increase of gas pressure.

The production of the *Joshi-Effect* in H_2 presents certain interesting features. Deshmukh[1] who sought to compare the relative magnitudes of the *Joshi-Effect* in various gases taken in the pressure range 25–35 mm. was led to the conclusion that the *Effect* varied in the order $Br_2 > O_2 >$ air $> N_2 > H_2$. In the present investigations, H_2 was taken in the pressure range 50–252 mm. For all pressures less than 252 mm., H_2 gave no *Joshi-Effect*. Even at 252 mm., there is no evidence of the more familiar negative *Joshi-Effect* (*cf.* Table II). At 3.4 kV the gas gives a large positive *Joshi-Effect*, *viz.*, 400% which declines rapidly to + 1.7% at 3.6 kV and then to zero

at higher potentials. It is of interest to emphasise that precisely similar results, *viz.*, a large positive *Joshi-Effect* at low applied potentials followed by a precipitous reversal to the negative *Joshi-Effect* by mere increase of the applied potential through a narrow range, were observed in air under an ozonizer discharge.

In Table III are given some typical data for the production of the *Joshi-Effect* in H_2, Br_2 mixtures. In the case where the partial pressure of H_2 is lower, positive *Joshi-Effect* is obtained at only one applied potential while in the other case the influence of H_2 becomes more pronounced and the mixture shows the positive *Joshi-Effect* over a wide range of applied potential.

The nature of the *Joshi-Effect* exhibited by Br_2 and H_2 taken alone and by their mixtures becomes explicable on the basis of considerations put forward by Joshi. According to him,[5, 6] 'electron affinity' of the excited gas is an important determinant of the negative *Joshi-Effect*. The observation that the relative magnitudes of the negative *Effect* shown at a particular potential by different gases is in the same order as their electron affinities lends support to such a view. It is known that the electron affinity of Br_2 which is a strongly electronegative gas is considerable while that of H_2 is low. It is to be anticipated that the behaviour of a mixture of the two gases in regard to the production of the *Joshi-Effect* should be modified by the relative proportion of the two gases.

Next, the influence, on the production of the *Joshi-Effect*, of 'ageing' H_2 in the discharge tube by exposing it to an applied potential of 0.40 kV for a certain number of hours was studied. The data are returned in Table IV. As remarked above, no *Joshi-Effect* was observed in H_2 upto 252 mm. But when H_2 at 50 mm. is 'aged' for three hours at 0.40 kV, the gas shows positive *Joshi-Effect* at low potentials and negative *Effect* at higher potentials. Further 'ageing' of the gas for another six hours results in the production of the positive *Effect* to a very much greater extent not only at potentials at which it earlier gave the negative *Effect* but also at higher potentials. Further 'ageings' of the gas produce larger and larger positive *Effect*. The trend of the values is that the positive *Joshi-Effect* shows the usual transition to the negative *Effect* but the potential at which this transition takes place is shifted higher after every 'ageing'.

The above results are significant and suggestive as regards the mechanism operating in the production of the *Joshi-Effect*. Joshi[3] has emphasised the importance of the part played by the walls of the reaction vessel in relation to the *Joshi-Effect*. A large amount of experimental data collected in these laboratories by various workers goes to show that a change in the wall surface

induced either by ' ageing ' or by coated materials exerts a profound influence on the nature and magnitude of the *Joshi-Effect*. An interesting reaction was observed in the ' ageing ' effect on Br_2 vapour[11] which showed a progressive decrease of conductivity at constant exciting potential. Discontinuance of the discharge for a few hours brought about only a partial restoration of the conductivity; full 24 hours were required to restore the conductivity to the initial value. The effect is attributed by Joshi to atomic and molecular bromine activated in the discharge and adsorbed on the walls of the discharge vessel. K. V. Rao[14] reports a similar observation regarding the role of the walls of the discharge tube. A mixture of Cl_2 and air admitted into the ozonizer was found to give large *Joshi-Effect*. Even when the mixture was toplered out and the ozonizer was filled with pure air only, the system gave equally large *Joshi-Effect*. On the other hand, when an ozonizer was merely filled with chlorine without energising it in the discharge and after exhausting it, filled with air, no *Joshi-Effect* was observed. K. V. Rao concludes that not mere sorption of neutral chlorine on the walls of the ozonizer but rather sorbed chlorine activated in the discharge is responsible for the production of the *Joshi-Effect*.

Equally suggestive are the results reported by Visvanathan and Rao regarding the influence of films of KCl, $BaCl_2$ and $HgCl_2$ given on the annular walls of the ozonizer on the nature and magnitude of the *Joshi-Effect* in air. $HgCl_2$ especially is found to give large positive *Joshi-Effect* in air at pressures for which the controlled (uncoated) ozonizer gave only a slight negative *Joshi-Effect*.

All these experimental observations are in accord with Joshi's views regarding the mechanism of the *Joshi-Effect*, *viz*., that the seat of the phenomenon is not in the homogeneous gas phase but on the walls of the ozonizer and that the formation of an activated electrode layer of the excited gas on the walls is a prerequisite for the production of the *Joshi-Effect*. The data in Table IV for the influence of ' ageing ' on the production of the *Joshi-Effect* in H_2 are in line with the findings above mentioned; it would also appear that the formation of the activated electrode layer of H_2 on the container walls is a time process whose rate probably depends on the potential at which ' ageing ' is effected.

In conclusion, the authors wish to express their grateful thanks to Prof. S. S. Joshi, University Professor and Head of the Chemistry Department, Benares Hindu University, for suggesting the problem, for kind interest and instructive discussions during the course of this work.

SUMMARY

The production and potential variation of the *Joshi-Effect* in Br_2 and H_2 and in mixtures of Br_2 and Cl_2 and of Br_2 and H_2 have been studied in the range 0.40–2.0 kV, 500 cycles frequency. The striking result was obtained, *viz.*, that Br_2, a strongly electronegative gas, at a pressure of 47 mm gives the positive *Joshi-Effect* at low potentials, which changes to the more familiar negative *Joshi-Effect* at higher potentials. The effect of admixing various quantities of Cl_2 with Br_2 is to mask the positive *Effect* completely and give the negative *Effect* only, which increases with increasing amounts of Cl_2.

H_2 at 252 mm gives the positive *Joshi-Effect* only while at lower pressures, neither negative nor positive *Effect* is obtained. The behaviour of mixtures of H_2 and Br_2 with regard to the production of the *Joshi-Effect* is determined by the relative proportion of the two gases. For a fixed quantity of Br_2, increasing the proportion of H_2 enhances the positive *Effect*.

While H_2 at 50 mm shows no *Joshi-Effect* at all, 'ageing' the gas in the ozonizer at 0.40 kV for three hours renders the system active. The gas now gives the positive *Joshi-Effect* initially and then at higher potentials the negative *Effect*, though only to a small extent. Further 'ageings' result in the production of larger and larger positive *Effect* even at those potentials at which the system gave earlier the negative *Effect*. The trend of the values shows that the potential at which the transition from the positive to the negative *Joshi-Effect* takes place is shifted higher with every 'ageing'. These results are highly suggestive in that they support Joshi's view regarding the mechanism that seems to operate in the production of the *Joshi-Effect*, *viz.*, that the *Effect* originates not in the homogeneous gas phase but on the walls of the reaction vessel. It would appear that the walls can be brought to that specially reactive condition suited to the production of the *Joshi-Effect* either by 'ageing' or by coating the walls with various substances.

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STUDIES ON THE DEPENDENCE OF OPTICAL ACTIVITY ON CHEMICAL CONSTITUTION

Part XXXI. The Rotatory Dispersion of Salts of Camphor-β-Sulphonic Acid with *o*-, *m*- and *p*-Iodanilines

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The present work is in continuation of our earlier work[1] and consists in the study of optical rotatory dispersion of camphor-β-sulphonates of *o*-, *m*- and *p*-iodanilines. Another object of this paper is to study the effect of substituting the electronegative element, iodine, for hydrogen in *o*-, *m*- and *p*-positions in the benzene ring of the anilinocamphor-β-sulphonates on the rotatory power of the resulting compounds and to compare its effect with that of chlorine when similarly substituted. As these are all primary amine salts, the occurrence of mutarotation, where it occurs, has been ascribed to the change of the structure of salt with the production of a ketamine or anil.

Influence of Wavelength on Rotatory Dispersion

The rotatory dispersion has been determined in the visible region of the spectrum for twelve wavelengths from λ 6708 Å.U. to λ 4358 Å.U. (Tables IV to VI). It is found to be "simple" as it obeys the one-term Drude's equation, $[\alpha] = \frac{k_0}{\lambda^2 - \lambda_0^2}$. In this equation ($K_0$), the "rotation constant" may be taken as the measure of absolute rotation for the wavelength λ for which $\lambda^2 - \lambda_0^2 = 1$ square micron. This value of λ is always in the infra-red and is slightly greater than 10,000 Å.U. The 'absolute' rotations (K_0) are thus numerically, but not dimensionally, identical with the magnitude of [α]. Comparison of rotatory power and rotation constant at this wavelength, where $\lambda = \sqrt{1+\lambda_0^2}$, may be regarded as those for corresponding conditions of wavelength, in which the effects of dispersion are eliminated.

The Physical Identity of Enantiomers

The rotatory power of *d*- and *l*-enantiomers (Tables IV to VI) are identical within the limits of experimental error and thus support Pasteur's law of Molecular Dissymmetry according to which the optical and their opposite isomers possess rotatory powers identical in magnitude but opposite

in sign. Out of 288 observations recorded in this paper in as many as 268 cases the differences between the observed and the calculated values of specific rotation correspond to a deviation of 0.02° or less in the observed angle of rotation, and in as many as 18 cases this deviation lies between 0.02° and 0.03°. Only in 2 cases, both for Hg 4358 (mercury violet)—a difficult line to read—this difference exceeds 0.03°. All these are, however, of the nature of casual experimental errors.

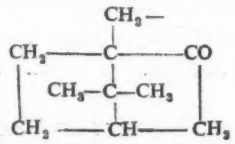
The Effect of Solvent on Rotatory Power

The order of decreasing rotatory power of the position isomerides (*o*-, *m*- and *p*-) of salts of iodanilinocamphor-β-sulphonates for Hg 5461 in different solvents is pyridine > ethyl alcohol > methyl alcohol > water (Table I), whereas the sequence of increasing dielectric constant of the

Table I

No.	Structural formula	$[\alpha]^{35°}_{5461}$			
		Water [80]*	Methyl Alcohol [31·1]	Ethyl Alcohol [25·8]	Pyridine [12·4]
1	†R·SO_3H·H_2N ..	20·50 (3·400)‡	32·40 (6·284)	36·40 (6·997)	36·10 (7·570)
2	R·SO_3H·H_2N ..	19·00 (3·110)	28·50 (5·254)	32·00 (6·037)	36·00 (7·216)
3	R·SO_3H·H_2N ..	2 ·00 (3·268)	28·00 (5·195)	33·00 (6·122)	34·50 (6·917)
4	R·SO_3H·H_2N ..	19·50 (3·207)	29·50 (5·357)	33·00 (6·310)	35·00 (7·077)

* The values in square brackets stand for the Dielectric Constant of the solvent.

† R = $C_{10}H_{15}O$ or 

‡ Values in brackets satnd for Rotation Constant K_0 (Absolute Rotation).

solvent is pyridine (12.4) < ethyl alcohol (25.8) < methyl alcohol (31.2) < water (80). Hence it is obvious that the sequence of dielectric constants of the solvents follows the same order as that of rotatory power but in the opposite sense.

As already pointed out in our previous work[2] it would, however, be more rational to compare the rotatory power of the solutions with their dielectric constants and not with the dielectric constants of the solvents.

The Molecular Rotatory Dispersion of Camphor-β-Sulphonates in Aqueous Solution and Comparison of the Value of $[M]_D^{35°}$ of Camphor-β-Sulphonate Ion in Water

Table II gives the values of $[M]_\lambda^{35°}$ for λ varying from 4358 Å.U. to 6708 Å.U., for the different camphor-β-sulphonates. If the salts were completely ionised in dilute aqueous solution, their molecular rotations would

Table II

No.	Camphor-β-sulphonates of	Concentrates in gm./100 cc.	Li 6708	Cd 6438	Li 6104	Na 5893	Hg 5780	Hg 5461	Ag 5209	Cd 5086	Cd 4800	Cd 4678	Li 4603	Hg 4358
1	1-Iodo 2-aminobenzene	0·5000	47·36	56·37	58·62	63·14	74·42	85·70	99·08	108·2	153·3	173·7	180·4	252·5
2	1-Iodo-3-aminobenzene	0·5000	49·62	56·37	63·14	67·66	72·16	90·20	106·0	121·8	151·1	175·9	184·9	266·2
3	1-Iodo-4-aminobenzene	0·5000	47·36	49·62	56·37	65·40	72·33	83·45	101·5	110·5	148·8	173·7	189·4	259·3

be practically the same for a given wavelength, the rotations being independent of the inactive basic ion: in concentrated solutions, the observed molecular rotation may be greater or less than the value in dilute solution, because it is due both to the active ion and to the non-ionised molecule. The mean value of $[M]_D^{35°}$ for the camphor-β-sulphonic ion is 53–54°.[3] The value of $[M]_D^{35°}$ for the salts of *o*-, *m*- and *p*-iodanilinocamphor-β-sulphonates is 63.14°, 67.66° and 65.40° respectively. As these values of the rotatory power of the salts are higher than the mean value of $[M]_D^{35°}$ of the camphor-β-sulphonate ion (53–54°) and as the observed molecular rotatory power of the salt in aqueous solution is the sum of the rotatory powers of the active acid ion and the non-ionised molecule, it is clear that the undissociated molecule has higher rotatory power and that these salts are not completely electrolytically dissociated in 0.5% aqueous solution.

Nature of the Racemic Modification

The melting point of the racemic modification of camphor-β-sulphonate of *o*-iodaniline is higher than those of its optical isomers. It is, therefore, a true *dl*-compound in the solid state. The melting points of the racemic forms of *m*-iodanilino-, and *p*-iodanilino-camphor-β-sulphonate are identical with those of their optical isomers. That the racemic forms of these salts

are also true *dl*-compounds was determined in the following way: a small amount of the *d*-form was added to the corresponding racemic modification in each case and the melting point of the mixture was found to be lowered. This clearly shows that these racemic camphor-β-sulphonates are also true *dl*-compounds.

The Effect of Position Isomerism on Rotatory Power

In Table A the order of rotatory power of position isomerides in different solvents for $[\alpha]^{15}_{5461}$ is given, the order of K*o* is also given in square brackets. On comparing the values of $[\alpha]^{35}_{5461}$, the sequence of position isomerides in

Table A

Solvent	$[\alpha]^{38°}_{5461}$
Water ..	$o < p < m < un$ $[o < p < m < un]$
Methyl alcohol ..	$m < o < p < un$ $[m < o < p < un]$
Ethyl alcohol ..	$o < m < p < un$ $[o < m < p < un]$
Pyridine ..	$m < p < o < un$ $[m < p < o < un]$

water is $o < p < m < un$, in methyl alcohol: $m < o < p < un$, in ethyl alcohol $o < m = p < un$ and in pyridine: $m < p < o < un$. Similar results follow when a comparison is made for the values of K_o. These results except in the case of ethyl alcohol do not agree with either Franklands' "lever-arm" hypothesis[4] or with its electrostatic modification as suggested by Rule,[5] according to both of which the *m*-isomer should be intermediate between *ortho* and *para* as regards its rotatory effect.

The Effect of Substituent Groups on Rotatory Power

Substituent groups may be arranged according to their polarities. Rule has shown that the arrangement of groups according to their polarities follows a general order, with minor differences, whether the order is deduced from benzene substitution data, the influence of various groups on dissociation constants of substituted acetic or benzoic acids or on the basis of electronic theory, and that the order is:

$$\overline{OH}\ Cl\ Br\ I\ Et\ Me\ \overset{+}{H}\ COOH\ CHO\ COCH_3\ CN\ \overset{+}{NO_2}$$

Since the effect of polar groups is traceable on rotatory power, it is found that in general the replacement of a hydrogen atom in an optically active

compound by a positive substituent displaces the rotation in the opposite sense to that due to a negative substituent, and further, in general, a positive group should increase the rotation and a negative group should cause a decrease in it. In Table III the values of $[\alpha]^{35°}_{5461}$ in different solvents are

TABLE III

No.	Camphor β-sulphonates of	$[\alpha]^{35}_{5461}$ in solvent			
		Water [80·1]*	Methyl Alcohol [31·1]	Ethyl Alcohol [25·8]	Pyridine [12·4]
1	Aniline[a]	20·50 (3·400)†	32·40 (6·284)	36·40 (6·997)	36·10 (7·570)
2	*o*-Nitroaniline[b] ..	..	29·97 (3·973)	29·50 (3·666)	31·96 (4·051)
3	*o*-Amino benzoic acid[c] ..	20·50 (3·560)	30·50 (5·950)	32·50 (6·271)	36·00 (7·123)
4	*o*-Toluidine[a] ..	19·87 (3·367)	29·60 (5·685)	34·74 (6·880)	36·20 (7·93)
5	*o*-Iodaniline ..	19·00 (3·110)	28·50 (5·254)	32·00 (6·037)	36·00 (7·216)
6	*o*-Chloraniline[d] ..	18·97 (3·078)	26·96 (4·251)	28·97 (5·058)	32·50 (5·379)
7	*m*-Nitroaniline[b] ..	..	34·47 (5·882)	35·38 (5·432)	35·97 (5·185)
8	*m*-Amino benzoic acid[c] ..	19·50 (3·555)	29·00 (5·697)	30·00 (5·618)	34·50 (6·953)
9	*m*-Toluidine[a] ..	18·80 (3·310)	28·90 (5·661)	34·10 (6·790)	35·50 (7·740)
10	*m*-Iodaniline ..	20·00 (3·268)	28·00 (5·195)	33·00 (6·122)	34·50 (6·917)
11	*m*-Chloraniline[d] ..	20·00 (3·644)	32·00 (6·386)	24·00 (6·945)	34·46 (6·541)
12	*p*-Nitroaniline[b] ..	..	30·47 (4·536)	30·42 (4·195)	31·42 (4·782)
13	*p*-Amino benzoic acid[c] ..	20·00 (3·475)	27·00 (5·113)	31·00 (5·777)	35·50 (7·139)
14	*p*-Toluidine[a] ..	20·20 (3·390)	30·47 (5·960)	35·50 (6·950)	37·60 (7·810)
15	*p*-Iodaniline ..	19·50 (3·207)	29·50 (5·357)	33·00 (6·310)	35·00 (7·077)
16	*p*-Chloraniline[a] ..	18·98 (3·510)	31·50 (6·276)	33·50 (6·689)	36·00 (6·420)

* The values in square brackets stand for the dielectric constant of the solvent.

† The values in brackets stand for Rotation Constant, K_0 (Absolute Rotation).

(*a*) Singh, B. K., *et. al*, *Proc. Lahore Phil. Soc.*, 1944, **6**, 15.

(*b*) Singh, B. K., and Perti, O. N., *Proc. Ind. Acad. Sci.* (A), 1945, **22**, 84.

(*c*) Singh, B. K., and Manhas, K. M. S., *ibid.*, 1945, **27**, 1.

(*d*) Singh, B. K., and Perti, O. N., *ibid.*, 1945, **22**, 265.

given. The values of K_0, the rotation constants, as above defined, are also given in brackets for the sake of comparison.

Ortho Substitution.—On comparing the values of $[\alpha]^{35°}_{5461}$ in water, it is found that CH_3, COOH, Cl and I groups cause a decrease in the rotatory power in the order COOH = H > CH_3 > I > Cl, whereas the order of

TABLE IV

o-Iodanilinocamphor-β-sulphonates

Solvent		Water		Methyl alcohol		Ethyl alcohol		Pyridine	
Concentration in gm./100 c.c.	*d-*	0·5000		1·0000		0·5000		1·0000	
	l-	0·5000		1·0000		0·5000		1·0000	
Calculated $[\alpha]_{\lambda_0}$		$\pm \frac{3\cdot11}{\lambda^2-0\cdot1346}$ 0·3669		$\pm \frac{5\cdot254}{\lambda^2-\cdot1139}$ 0·3375		$\pm \frac{6\cdot077}{\lambda^2-\cdot1095}$ 0·3310		$\pm \frac{7\cdot216}{\lambda^2-0\cdot0976}$ 0·3124	
Line		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
		d-	*l-*	*d-*	*l-*	*d-*	*l-*	*d-*	*d-*
Hg_{4358}	..	+56·00°	−53·50	+68·00	−69·00″	+75·50°	−75·00°	+79·00°	−76·50°
Li_{4603}	..	40·00	39·00	53·50	54·50	57·50	59·50	62·50	64·50
Cd_{4678}	..	38·50	36·50	51·00	50·50	54·50	55·50	60·00	59·00
Cd_{4800}	..	34·00	32·50	45·00	46·00	47·50	48·00	55·50	53·50
Cd_{5086}	..	24·00	26·00	37·00	37·00	41·50	41·50	44·00	45·00
Ag_{5209}	..	22·00	22·50	33·50	33·00	39·00	40·00	40·50	42·00
Hg_{5461}	..	19·00	19·50	28·50	29·00	32·00	31·50	36·00	36·00
Hg_{5780}	..	16·50	16·50	24·00	23·50	26·00	26·00	30·50	30·00
Na_{5893}	..	14·00	15·50	22·50	22·50	25·50	23·50	28·50	28·00
Li_{6104}	..	13·00	12·50	20·50	20·50	23·50	23·00	26·50	27·00
Cd_{6438}	..	12·50	12·00	17·00	18·00	19·00	20·50	21·50	20·50
Li_{6708}	..	10·50	11·50	14·50	15·00	17·50	16·50	19·00	19·50

decreasing value of K_0 is COOH > H > CH_3 > I > Cl. Thus the groups CH_3, I and Cl behave in the opposite sense from COOH, in conformity with the above mentioned polar series. This, however, does not hold good in other solvents: In methyl alcohol and ethyl alcohol it is found that the substituent groups CH_3, I, Cl, COOH and NO_2 cause a decrease in the values of both $[\alpha]^{35°}_{5461}$ and K_0. The order for $[\alpha]^{35°}_{5461}$ in methyl alcohol is H > COOH > NO_2 > CH_3 > I > Cl and for K_0, H > COOH > CH_3 > I > Cl > NO_2. The order for $[\alpha]^{35°}_{5461}$ in ethyl alcohol is H > CH_3 > COOH > I > NO_2 > Cl and for K_0, H > CH_3 > COOH > I > Cl > NO_2. In neither case it agrees with the above mentioned polar series of the substituent groups.

However, on comparing the values of $[\alpha]^{35°}_{5461}$ in pyridine, it is found that the order for decreasing rotatory power is CH_3 > H > COOH = I > Cl > NO_2 and for K_0 the order is CH_3 > H > I > COOH > Cl > NO_2. This follows the order of polarity except in the cases of halogen substitution,

Meta substitution.—On comparing the values of $[\alpha]^{25°}_{5461}$ in water, the order of decreasing rotatory power is $H > Cl > I > COOH > CH_3$, in methyl alcohol $NO_2 > H > Cl > COOH > CH_3 > I$, in ethyl alcohol $H > NO_2 > CH_3 > Cl > I > COOH$ and in pyridine $H > NO_2 > CH_3 > COOH > I > Cl$. In none of these cases the order agrees with that of polar series. On comparing the values of K_0 it is, however, found that in water the order is $Cl > COOH > H > CH_3 > I$ which is in conformity with the polar series except for Cl. In pyridine the sequence is $CH_3 > H > COOH > I > Cl > NO_2$ where Cl and I stand out of the polar order. In methyl alcohol and ethyl alcohol the order is $Cl > H > NO_2 > COOH > CH_3 > I$ and $H > Cl > CH_3 > I > COOH > NO_2$ respectively which does not agree with the above mentioned polar series.

TABLE V

m-*Iodanilinocamphor-β-sulphonates*

Solvent		Water		Methyl alcohol		Ethyl alcohol		Pyridine	
Concentration in gm./100 c.c.	*d*-	0·5000		1·0000		0·5000		1·0000	
	l-	0·5000		1·0000		0·5000		1·0000	
Calculated $[\alpha]$		$\pm \frac{3·268}{\lambda^2 - ·1342}$		$\pm \frac{5·135}{\lambda^2 - ·1123}$		$\pm \frac{6·122}{\lambda^2 - ·1119}$		$\pm \frac{6·917}{\lambda^2 - 0·9774}$	
Calculated λ_0		0·3564		0·3351		0·3345		0·3127	
Line		Obs. [α]		Obs. [α]		Obs [α]		Obs. [α]	
		d-	*l*-	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-
Hg_{4358}	..	+59·00°	−60·50°	+66·00°	−67·00°	+79·50°	−76·00°	+75·00°	−73·00°
Li_{6403}	..	41·00	42·50	51·50	60·00	60·00	60·50	60·00	62·00
Cd_{4678}	..	39·00	40·00	49·00	48·00	56·50	56·50	56·50	56·50
Cd_{4800}	..	32·50	33·50	44·50	44·00	50·50	52·50	51·50	52·50
Cd_{5086}	..	27·00	25·00	36·00	34·50	40·00	40·50	43·00	42·50
Ag_{5209}	..	23·50	24·00	32·50	32·50	37·00	39·00	40·00	40·50
Hg_{5461}	..	20·00	20·00	28·00	28·00	33·00	32·50	34·50	34·50
Hg_{5780}	..	16·00	17·00	24·50	23·50	28·00	28·50	28·50	30·00
Na_{5893}	..	15·50	16·50	22·00	22·00	24·50	25·50	28·00	28·50
Li_{6104}	..	14·00	13·50	20·00	20·50	22·50	24·00	25·50	25·00
Cd_{6438}	..	12·50	13·00	17·00	17·50	21·00	21·50	20·50	21·00
Li_{6708}	..	11·00	11·50	14·00	15·50	19·00	19·50	19·00	19·00

Para substitution.—

The order of $[\alpha]^{25°}_{5461}$ in water in the case of para substitution, is $H > CH_3 > COOH > I > Cl$, in methyl alcohol $H > Cl > NO_2 = CH_3 > I > COOH$, in ethyl alcohol $H > CH_3 > Cl > I > COOH > NO_2$ and in pyridine $CH_3 > H > Cl > COOH > I > NO_2$. In the case of water,

methyl alcohol and ethyl alcohol the sequence does not correspond to the polar series but in pyridine it agrees except for Cl and I.

The comparison of the values of K_0 shows that the order in water is $Cl > COOH > H > CH_3 > I$, in methyl alcohol $H > Cl > CH_3 > I > COOH > NO_2$, in ethyl alcohol $H > CH_3 > Cl > I > COOH > NO_2$ and in pyridine $CH_3 > H > COOH > I > Cl > NO_2$. Thus the results are in conformity with the polar series in water and pyridine, except for halogens.

TABLE VI

p-iodanilinocamphor-β-sulphonates

Solvent	Water		Methyl alcohol		Ethyl alcohol		Pyridine	
Concentration in gm./100 c.c.	*d*- 0·5000	*l*- 0·5000	1·0000	1·0000	0·5000	0·5000	0·1000	0·1000
Calculated [α]	$\pm \frac{3\cdot207}{\lambda^2 - \cdot1338}$		$\pm \frac{5\cdot357}{\lambda^2 - \cdot1166}$		$\pm \frac{6\cdot31}{\lambda^2 - \cdot1070}$		$\pm \frac{7\cdot077}{\lambda^2 - \cdot0955}$	
Calculated λ_0	0·3658		0·3415		0·3271		0·3090	
Line	Obs. [α]		Obs. [α]		Obs [α]		Obs. [α]	
	d-	*l*-	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-
Hg_{4358} ..	+57·50°	−57·00	+74·50	−71·50°	+78·50°	−76·00°	+75·00°	−76·00°
Li_{6403} ..	42·00	41·00	57·00	56·50	62·50	61·50	60·00	61·00
Cd_{4678} ..	38·50	37·50	52·50	52·50	57·50	57·00	58·00	57·00
Cd_{4800} ..	33·00	33·50	47·00	47·00	50·50	52·00	52·00	52·00
Cd_{5086} ..	24·50	25·50	36·50	38·00	40·00	40·50	43·00	43·50
Ag_{5209} ..	22·50	22·00	34·50	34·00	37·50	37·00	40·50	40·00
Hg_{5461} ..	18·50	20·00	29·50	29·00	33·00	33·50	35·00	35·00
Hg_{5780} ..	16·00	16·50	24·50	24·50	20·00	27·50	29·50	29·00
Na_{5893} ..	14·50	15·00	23·00	24·00	27·00	26·50	28·00	28·50
Li_{6104} ..	12·50	13·50	21·00	20·50	23·50	22·50	25·50	25·00
Cd_{6438} ..	11·00	11·50	18·50	17·50	22·00	19·50	23·50	23·00
Li_{6708} ..	10·50	10·50	17·00	16·50	19·50	19·00	20·50	20·50

The order in methyl alcohol and ethyl alcohol does not agree with the polar series at all.

It is, therefore, clear as stated in our previous communication that a better agreement is found with the above mentioned polar series of substituent groups for the values of K_0, the absolute rotation constant, and not for the values of $[\alpha]^{35°}_{5461}$, the specific rotatory power for an arbitrary wavelength. The positive groups, COOH and NO_2, in the polar series, behave similarly and opposite to the negative CH_3 group. It is also evident that greater accord in rotatory power with the polar effect is found in the cases of ortho substituents as might be expected from the closer proximity of the

groups to the asymmetric centre in the molecule and is in conformity with our previous observations.[1]

Experimental

Preparation of o-, m- and p-iodanilinocamphor-β-sulphonates.—Molar proportions of the base (*o*-, *m*- and *p*-iodanilines) and the camphor-β-sulphonic acid (*d*-, *l*- and *dl*-form) were dissolved separately in hot ethyl acetate. The two solutions were mixed and allowed to stand when the salt crystallised out. They were then repeatedly recrystallised from absolute ethyl alcohol and dried in vacuum. These salts are fairly soluble in methyl alcohol and pyridine, less so in water and ethyl alcohol but practically insoluble in chloroform, acetone and benzene.

Salts of *d*-, *l*- and *dl*-camphor-β-sulphonic acid with		Crystalline structure	Found		Calculated Sulphur %
			M.P.	Sulphur %	
o-Iodaniline	*d*-salt ..	Fine prisms	260°*d*.	6·28	6·35
	l-salt ..	do	260–261°*d*.	6·15	do
	dl-salt ..	do	270°*d*.	6·19	do
m-Iodaniline	*d*-salt ..	Transparent plates	172° C.	6·50	do
	l-salt ..	do	172° C.	6·16	do
	dl-salt ..	do	172° C.	6·43	do
p-Iodaniline	*d*-salt ..	White-needles	165–169° C.	6·53	do
	l-salt ..	do	165–168° C.	6·57	do
	dl-salt ..	do	167–170° C.	6·28	do

The rotatory power determinations were made in a 2-dcm. tube. All the observations of rotatory power were carried out at approximately 35° C. The values of λ_0, calculated from the dispersion formulæ, are given in Tables IV to VI and are expressed as μ or 10^{-4} cm.

Summary

1. The rotatory dispersion of stereoisomeric salts of *o*-, *m*- and *p*-iodanilines with camphor-β-sulphonic acids is found, in different solvents, to obey Drude's one-term equation, $\alpha = \frac{k_0}{\lambda^2 - \lambda_0{}^2}$; it is therefore simple.

2. The *d*- and *l*- forms of these compounds possess identical rotatory power within the limits of experimental error and thus further support Pasteur's Law of Molecular Dissymmetry.

3. The sequence of rotatory power in different solvents runs exactly in the reverse order of the dielectric constants of the solvents.

4. The influence of iodine on rotatory power has been discussed and is found to depress it.

5. The effect of position isomerism on rotatory power has also been discussed.

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